

CRREL

REPORT 85-18



12

US Army Corps
of Engineers

Cold Regions Research &
Engineering Laboratory

Sorption of military explosive contaminants on bentonite drilling muds

AD-A163 231

FILE COPY

DTIC
ELECTE
JAN 22 1986
S D D

For conversion of SI metric units to U.S./British customary units of measurement consult ASTM Standard E380, Metric Practice Guide, published by the American Society for Testing and Materials, 1916 Race St., Philadelphia, Pa. 19103.

Cover: Scanning electron micrograph of Quik-Gel particles ($\times 25,000$). (Photograph by M. Kumal.)

CRREL Report 85-18

November 1985



Sorption of military explosive contaminants on bentonite drilling muds

Daniel C. Leggett

Accession For	
NTIS CRA&I	<input checked="checked" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By	
Distribution /	
Availability Codes	
Dist	Availability or Special
A-1	

Prepared for
U.S. ARMY TOXIC AND HAZARDOUS MATERIALS AGENCY
REPORT AMX-TH-TE-TR-85040

Approved for public release; distribution is unlimited.




SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

* SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

20. Abstract (cont'd)

concentration is known. Isotherms for TNT and DNT were not linear, however. Scatchard analysis suggested that the isotherms for these analytes could be resolved into two predominant components: a linear component above a certain sorbed quantity and a Langmuir-type component below this quantity. The experimental data were fitted by regression analysis using the appropriate model. The equations developed can be used to predict the sorbed fraction (analytical bias) for any combination of solids and analyte concentration. The amounts of bentonite found in some existing wells do not appear to be sufficient to cause significant bias in analyses for these explosive contaminants.



PREFACE

This report was prepared by Daniel C. Leggett, Research Chemist, Earth Sciences Branch, Research Division, U.S. Army Cold Regions Research and Engineering Laboratory. A number of others are acknowledged gratefully for their contribution to this effort. Brian Foley was responsible for the isotherm measurements. Dr. Joseph Oliphant provided the routine for non-linear regression of the data in this report. Dr. Motoi Kumai did the SEM/EDXA analyses. Eleanor Huke prepared the figures. Nancy Richardson typed the manuscripts. Allen Tice donated the Wyoming bentonite sample and Thomas Jenkins the well water used in the experiments.

The Quik-Gel and Aqua-Gel bentonite samples used in most of the experiments were donated by Baroid Corporation through Ray Morris, Product Line Manager. Mr. Jenkins and Dr. Oliphant reviewed the manuscripts for technical content. David Cate edited the final manuscript.

The U.S. Army Toxic and Hazardous Materials Agency (THAMA) provided the funding for this work. Dr. L. Eng of THAMA provided managerial support and technical guidance throughout the project. John Sanda of THAMA provided technical guidance and reviewed the report. M. Stutz reviewed the report and provided the official permission to publish the report for that agency.

The contents of this report are not to be used for advertising or promotional purposes. Citation of brand names does not constitute an official endorsement or approval of such commercial products.

CONTENTS

	Page
Abstract	i
Preface	iii
Introduction	1
Materials and methods	3
Bentonite and water samples	3
Sorbate solutions	4
Sorption isotherms	4
HPLC analysis	4
Analyte standards	4
Water solubilities	4
Octanol-water partition coefficients	4
Sorption isotherms	5
Freundlich	5
Langmuir	5
BET	5
Scatchard	5
Gibbs	6
Linear	6
Polynomial	6
Results and discussion	6
TNT	6
DNT	9
RDX and HMX	10
Effect of drilling muds on analysis	11
SEM and EDXA analysis of bentonite wells	11
Other studies	12
Summary	13
Literature cited	14
Appendix A: Results for TNT	17
Appendix B: Results for DNT	25
Appendix C: Results for RDX	28
Appendix D: Results for HMX	31
Appendix E: Characteristics of Quik-Gel, Aqua-Gel and well water	33

TABLES

Table

1. Least-squares estimates of equilibrium constants for TNT on bentonite drilling muds	7
2. Least-squares estimates of equilibrium constants for DNT on bentonite drilling muds	10
3. Least-squares estimates of equilibrium constants for RDX and HMX on bentonite drilling muds	10
4. Octanol-water partition coefficients and equilibrium constants of explosive contaminants at $23^{\circ} \pm 2^{\circ}\text{C}$	12
5. Water solubilities of explosive contaminants	12
6. Predicted and measured octanol-water partition coefficients for explosive contaminants	13

SORPTION OF MILITARY EXPLOSIVE CONTAMINANTS ON BENTONITE DRILLING MUDS

Daniel C. Leggett

INTRODUCTION

The Army has been manufacturing explosives for more than 40 years, but only recently has there been a significant effort to assess the impact of these materials on the environment. Concern about the environmental fate of these contaminants has brought about development of sensitive analytical techniques for measuring these substances in water. Monitoring wells are customarily installed at explosive manufacturing facilities to enable detection of contaminants in groundwater.

Protocols for groundwater sampling including the drilling and development of wells for monitoring purposes have been prepared (THAMA 1982, 1983). In drilling these wells, contractors are permitted to use muds consisting of pure bentonite clay. This policy raises several questions regarding the validity of groundwater analyses from wells drilled with bentonite. Recovery of bentonite from the drilling process is incomplete or unknown (THAMA 1980), and reduced permeability of the aquifer material around the drill hole has been attributed largely to invasion by drilling mud (Dudgeon and Cox 1976, Dudgeon and Huyakorn 1976). Residual mud around the well screen could lead to reduced contaminant recovery by adsorption. Also, fine particles may remain suspended in the water column for some time after develop-

ment, or resuspension may occur during sampling. This could also lead to reduced contaminant recovery, particularly if the water sample is filtered prior to analysis. Third, the drilling muds may release contaminants into the water which interfere with the analysis.

Studies of sorption of organic compounds on clay minerals are too numerous to mention here. However, a search of the Chemical Abstracts Data Base since 1967 (Dialog) for items dealing with sorption of explosive compounds on clays was negative. Nor were any recorded for sorption of other organic compounds on drilling muds specifically, although the some 1270 items located by the search were carefully scanned.

The sponsor of this work made available one unpublished study of explosive sorption by a drilling mud (Yurow and Tarantino 1980). Since the data were limited and the experimental procedure involved flocculation with strong acid and very short equilibration times, it appeared desirable to conduct a more extensive set of measurements under more natural conditions.

Related information dealing with sorption of explosives on soils and sediments is available in several government contractor reports (Hale et al. 1979, Sikka et al. 1980, Spanggord et al. 1980). This information is useful but the role of clay minerals in these samples cannot be deduced because

coating by natural organic matter masks the adsorptive capacity the clay would have if it were alone.

Sorption of polar organics on clays has been studied extensively, and several reviews of the subject are available (e.g. Mortland 1970, Theng 1974). It is often suggested that interaction with electronegative groups occurs by hydrogen bonding through coordinated water (Yariv et al. 1966, Parfitt and Mortland 1968, Fusi et al. 1982, Grauer et al. 1983). This is substantiated by infrared data using relatively high sorbate concentrations, frequently in partially dehydrated clays. Whether the sorption mechanism is the same for dilute aqueous sorbent-sorbate systems remains open to question. The few thermodynamic data available for dilute aqueous systems suggest an electrostatic bonding mechanism of some sort at low surface coverage (Haque and Coshov 1971, Bansal et al. 1982). The four explosive compounds considered here appear to have abundant potential for hydrogen bonding and dipole interactions, particularly TNT and DNT, because the polarity of the aromatic nitro group is enhanced by intramolecular charge transfer (Leermakers et al. 1966, Yariv et al. 1966).

TNT also forms charge-transfer complexes with nucleophiles, such as hydroxyl and alkoxyl ions in solution (Terrier 1982), and is a classic Lewis acid (electron-pair acceptor) like trinitrobenzene (Lewis and Seaborg 1940, Jensen 1982) because of the electron-withdrawing strength of three nitro groups on a single aromatic nucleus. Lewis acid-base interactions are common on clay minerals and form the basis for much of their catalytic activity (Solomon 1968). Dry montmorillonite (bentonite) has Lewis acid sites at Al and Fe edges, which become Bronsted acids (H donors) when hydrated. In aqueous systems, hydrogen bonding will probably occur between oxygens of the nitroaromatics and hydrated Al and Fe (edge) groups or hydrated cations of the clay (Yariv et al. 1966, Fusi et al. 1982).

Whether nonspecific hydrophobic effects also contribute to the transfer of neutral organics from aqueous solutions to pure mineral surfaces is not yet clear. Hydrophobic (poorly water soluble) organic compounds are transferred to organic surfaces and natural soils by a mechanism that is largely entropic (Leo et al. 1971, Schwarzenbach and Westall 1981, Voice and Weber 1983, Wauchope and Koskinen 1983). This appears to be analogous to the partitioning between water and immiscible solvents, which has a large entropy contribution (e.g. Leo et al. 1971, Arakawa et al. 1979,

Tanford 1980, Goffardi and Liveri 1981). The entropy effect is thought to be due to the cohesive energy of water; therefore, the type of surface or bulk phase with which it is in contact should not significantly affect the transfer. This assumption is supported by theoretical calculations for a number of organic surfaces (Dexter and Pavlov 1978). However, when there are relatively strong water-surface interactions, as for clays and other minerals such as silica gel (Dexter and Pavlov 1978), the assumption that sorption is controlled by entropic effects may not be valid.

The solvent used most often for hydrophobic effect correlations is n-octanol, and a large compilation of octanol-water partition coefficients is available (Hansch and Leo 1979). Partition coefficients in other solvent-water systems are then correlated using linear free-energy relationships (Leo et al. 1971) and are quite similar when corrected for water in the organic phase (Briggs 1981). This concept has been extended to organic surfaces (Leo et al. 1971), and more recently to soils and sediments, by using the weight fraction of organic matter or organic carbon as a normalization factor (Karickhoff et al. 1979, Means et al. 1980, Briggs 1981, Karickhoff 1981, Schwarzenbach and Westall 1981, Chiou et al. 1983). Correlations are generally good.

Linear free-energy correlations for various inorganic surfaces have not been conducted, although there are abundant data to attempt such a correlation. One study did show a high correlation between octanol-water, alumina-water, and kaolinite-water distribution* coefficients (Schwarzenbach and Westall 1981), suggesting that such efforts would indeed be worthwhile. Other evidence also suggests that sorption on clays may be hydrophobic: 1) increased equilibrium constants as chain length increases in a homologous series (Meyers and Oas 1978, Sullivan et al. 1982), 2) very large

*Terms should be chosen carefully because confusion can arise by calling sorption equilibrium constants "partition coefficients." I prefer to lump all types of equilibrium constant under the term "distribution coefficient" and reserve "partition coefficient" to mean distribution between two bulk phases. This is not just a semantic problem, as the notion persists that sorption on soil organic matter is like, or is in fact, a partitioning between it and water (Chiou et al. 1979, 1983, Briggs 1981). This is apparently because of the high correlation with octanol-water partition coefficients and the fact that the two processes are often mathematically indistinguishable. The same functional similarities were observed for alumina and kaolin containing virtually no organic matter, however (Schwarzenbach and Westall 1981). This and other arguments against the tenability of the partitioning concept as it applies to soil organic matter have recently been aired (Mingelgrin and Gerstl 1983).

equilibrium constants for hydrophobic compounds for which no other sorption mechanism is apparent (Pierce et al. 1974, Sullivan et al. 1982, Horzempa and DiToro 1983), and 3) ionic strength effects, discussed below.

A review of the literature suggested several factors that should be considered in assessing sorption effects on explosives analyses: solids concentration, reversibility, ionic strength, temperature and pH. Several recent reports suggest that the concentration of adsorbing solids controls the observed equilibrium ratio of sorbate between the solution and solid phases (O'Connor and Connolly 1982, Horzempa and DiToro 1983, Voice et al. 1983). Generally, an inverse relationship is found between distribution ratio and solids concentration. This effect has not yet been adequately explained but has obvious implications for extrapolating information obtained in the laboratory to the real world. For this reason it is desirable to include as wide a range of sorbent concentrations as technically possible.

Ideally, physical sorption equilibria are characterized by complete reversibility; i.e. sorption and desorption isotherms should be identical. However, for many real sorbent-sorbate systems where this was studied, sorption was not completely reversible (Hamaker and Thompson 1972, Wildish et al. 1980, DiToro and Horzempa 1982, Sullivan et al. 1982). This effect is apparently more frequently observed in organic sediments but was also reported for clay minerals. The reasons for apparent irreversibility are also not well understood, but in some cases it may be due to chemical reaction, failure to reach equilibrium, or slow desorption kinetics. Irreversible sorption and/or degradation has been reported for TNT in sediments (Fusi et al. 1982, Grauer et al. 1983). Thus it seems important to determine if explosive compounds are reversibly sorbed onto bentonite.

Groundwater contains varying amounts of dissolved solids, which determine its ionic strength. Equilibrium distribution ratios of neutral organics between soil components and water increase with ionic strength (Karickhoff et al. 1979, Wildish et al. 1980, Chou et al. 1982, Sullivan et al. 1982). This is similar to its effect on solubility and solvent-water partition coefficients, the familiar salting-out effect. The effect is negligible except at very high salt concentrations, so it would not be expected to affect sorption from nonestuarine groundwater onto bentonite. The fact that sorption on bentonite (montmorillonite) is increased by dissolved salts (Sullivan et al. 1982, Horzempa and DiToro 1983) is further evidence of hydropho-

bic bonding in clay-water systems, although other explanations are also possible (Hamaker and Thompson 1972).

Equilibrium constants controlled by all types of physical-electrostatic interactions between sorbates and sorbents should be inversely related to temperature. However, sorption on hydrophilic surfaces such as clay minerals may often be an exchange process, with adsorbed water (Mortland 1970, Gerstl and Mingelgrin 1979) making the temperature dependence more complicated. Also, changes in sorbent and/or sorbate conformation with temperature could facilitate adsorption. Increasing the temperature may also supply the activation energy needed to complete diffusion-controlled equilibrium (Hamaker and Thompson 1972). Technically some systems may not reach thermodynamic equilibrium within the practical time constraints of experimentation (Freeman and Cheung 1981, Wauchope and Koskinen 1983). If hydrophobic effects dominate the sorption process, temperature may increase, decrease, or have no effect on sorption (Pierce et al. 1974, Chiou et al. 1979, Weber et al. 1983). Thus, while the effect of temperature over the narrow range encountered in groundwaters is expected to be small, a priori judgements cannot be made for the bentonite-water-explosive contaminant systems.

Bentonite has cation exchange properties. Therefore, pH will profoundly affect sorption of cations other than hydrogen. Anions and neutral molecules should not be so affected, although hydrogen bonding interactions may be facilitated at low pH. In the range of normal groundwater pH we would not expect an effect on sorption of neutral species.

In the work reported here I have chosen to concentrate on solids concentration, ionic strength, and reversibility. Temperature, while interesting from a thermodynamic point of view, was expected to have little effect over the range expected in the field; the same is true of pH. These were not extensively studied in the experiment.

MATERIALS AND METHODS

Bentonite and water samples

Bentonite drilling muds, Aqua-Gel and Quik-Gel, were obtained from Baroid Corp., Houston, Texas. They were used as received. The chemical and physical analyses provided by the supplier are shown in Tables E1 and E2. A reference sample of Wyoming bentonite, saturated with Na and sieved to $< 149 \mu\text{m}$, was used to establish a baseline for

"natural" bentonite. Well water was obtained from a private well in Canaan, New Hampshire. Analyses are shown in Table E3. Other diluents for preparing bentonite suspensions were distilled water, 0.05 M NaCl and 0.05 M MgCl, prepared from reagent grade chemicals.

Sorbate solutions

Sorbate solutions were prepared from the saturated analyte solutions used to determine solubility after filtration and serial dilution in well water. Seven concentrations plus a water blank were usually prepared; 1.00 mL of each was used for spiking the tubes containing bentonite suspensions. The various initial concentrations used for the different analytes are shown in Tables A1-D2. Generally one or more of the dilutions was near or below the detection limit of the high-performance liquid chromatography (HPLC) method.

Sorption isotherms

Bentonite samples were weighed to the nearest 0.1 mg into Pyrex culture tubes, and 5.00 mL of well water or amended well water were added. After the tubes were capped, the bentonite was dispersed by hand shaking, and then allowed to stand overnight in a refrigerator (4°C). To these tubes were added 1.00-mL spikes of one of the four analyte solutions, and the tubes were shaken on a wrist-action shaker for 2 hours in a 10°C cold-room in the dark. They were then centrifuged at 7500 rpm (6300 g) for 1 hour at 10°C. This velocity was calculated from Stokes Law to be sufficient to spin down 0.1- μ m particles sufficiently for sampling of the supernatant. The supernatants all had a visually clear zone, which was then sampled with a 500- μ L syringe for direct injection into a liquid chromatograph. The temperature of the tubes was maintained at 10°C until the supernatant was removed.

For desorption isotherms the tubes were weighed and as much as possible of the supernatant removed without disturbing the gel phase. The tubes were reweighed, and the exact amount of the diluent was added back to equal the amount removed. The amount of original solution remaining with the gel was calculated by difference. This was used to correct the sorbed concentration by the amount retained in gel water to obtain an initial mass of sorbate for desorption. The correction was necessary because the amount of solution retained by the gel was significant. I also attempted to determine the extent of sorption on the glass culture tubes, but the amount sorbed was less than the precision of the method. Small positive and nega-

tive amounts of "sorption" were observed at different times, suggesting that it was an artifact of the method and would not bias the results.

HPLC analysis

Analyses of the supernatants were performed in duplicate. A Perkin-Elmer LC-65T variable-wavelength detector set at 254 nm was used in conjunction with a Perkin-Elmer Series 3B pumping station and a Rheodyne 7125 valve with 100- μ L loop injector. The loop was used in the complete-fill mode by flushing it with 400-500 μ L of the supernatant. The analytical column was 250 by 4.6 mm packed with 5 μ m of LC-8 reverse-phase material from Supelco. The mobile phase for TNT and DNT was generally methanol and water (60:40). For RDX and HMX, a solution of water, methanol and acetonitrile (50:38:12) was used. The flow rate was 1.5 mL/min. All analyses were conducted at ambient temperature (23° \pm 2°C).

Analyte standards

Analyte standards for quantitative analysis by HPLC were prepared from Standard Analytical Reference Materials (SARM) used as received. Stock solutions of each analyte were prepared in methanol or acetonitrile and methanol. A combined analyte was prepared by diluting these stocks with methanol. A working standard was prepared by diluting the combined analyte with HPLC water. The final concentrations were TNT, 226 μ g/L; DNT, 271 μ g/L; RDX, 488 μ g/L; HMX, 614 μ g/L. One-point calibration curves were prepared by injecting the working standard several times during each day that samples were analyzed. The required linearity and zero intercept have been documented (Jenkins et al. 1984).

Water solubilities

TNT and DNT were obtained from Eastman Kodak and military grade RDX from U.S. Army MERADCOM (formerly MERDC). Saturated solutions were prepared at 23° \pm 2°C by stirring a ten-fold excess of each with 500 mL of well water for 16 hours on a magnetic stirrer. A 10-mL portion of each solution was then filtered using a syringe filter composed of a B-D plastic syringe, a Nuclepore polycarbonate filter holder, and a 0.1- μ m Nuclepore polycarbonate membrane. A second 10.0-mL portion was filtered and diluted to 100 mL with well water for HPLC analysis.

Octanol-water partition coefficients

A 10.0-mL aliquot of the saturated TNT, DNT or RDX solution prepared above was added to a

separatory funnel containing 10.0 mL of Baker reagent 1-octanol. The separatory funnel was stoppered and shaken vigorously by hand for about 60 seconds. One hour was allowed for phase separation. Then the water phase was filtered, first through glass wool and then through a 0.1- μ m polycarbonate filter. The filtrate was analyzed directly by HPLC, and the concentration in the octanol was calculated by the difference between initial (saturation) and final concentrations. The partition coefficients obtained were corrected for the mutual solubility of water in octanol and octanol in water. No change in volume on mixing was assumed, giving final corrected volumes for water and octanol of 9.586 and 10.414 mL, respectively. HMX was determined from its impurity peak in RDX.

SORPTION ISOTHERMS

Sorption data are generally reported using one of the various types of sorption isotherms. There is considerable disagreement in the literature on the best way to model and interpret experimental data, with the result that no one isotherm is acceptable for all types of data. Voice and Weber (1983) recently presented a good discussion of sorption isotherms.

Freundlich

This is probably the isotherm most widely used in representing sorption at the solid/liquid interface. It is a versatile equation for representing data covering a wide range of concentrations in the log-log form:

$$C_s = KC_e \quad (1)$$

$$\log C_s = n \log C_e + K$$

where C_s and C_e are equilibrium sorbed and solution concentrations, respectively. Thus n is the slope and K the intercept of the plot. Despite its usefulness and widespread use, it is deficient in many respects. It is largely an empirical device and theoretical interpretation is difficult [see Wauchope and Koskinen (1983), however]. Because of the nature of log-log plots the data fit appears better than it is. The K value is not singular and depends on the system of units used (Bowman 1981).

Langmuir

Originally developed for gas-solid work, this isotherm can be used for liquids in some cases. It

assumes that surface coverage is limited to one monolayer with uniform interaction energy and no sorbate-sorbate interaction. These conditions are seldom met in reality. The equation is derived from mass action laws and is thermodynamically sound:

$$C_s = \frac{KnC_e}{1 + KC_e} \quad (2)$$

where C_s and C_e are as before, n is the maximum possible surface coverage corresponding to one monolayer, and K is a constant. Various linear transformations are used to treat experimental data (Voice and Weber 1983). Note that when C_e is large, $C_s = n$ is constant; when C_e is small, $C_s = KnC_e$, and the isotherm is linear. It is the latter case that is of most interest for environmental applications involving sorption of poorly soluble chemicals from water.

BET

An extended form of the Langmuir equation, this isotherm allows for multilayer surface coverage. Subsequent layers can begin forming before monolayer coverage is complete. Each layer can have different sorption energies (Voice and Weber 1983). It too reduces to a linear equation at low surface coverage, which is likely for many contaminant problems [see Dexter and Pavlov (1978) for an application].

Scatchard

Originally derived for protein binding measurements (Scatchard 1949), this is a linear form of a mass action isotherm like the Langmuir and BET with some of the restrictions removed. It considers all discrete classes of sites, not necessarily monolayers. In fact, Langmuir and BET are subsets of this general isotherm and can be treated by the Scatchard method. It is most useful in resolving two or more classes of sorption sites having distinct differences in energy. The Scatchard equation is

$$C_s/C_e = K(n - C_s) \quad (3)$$

where the terms are the same as for Langmuir sorption except that n may or may not correspond to monolayer coverage, and both n and K may be multivalued since there is a characteristic n, K pair for each distinct class of binding site.

C_s/C_e is plotted against C_s . The extrapolated intercept at $C_s = 0$ is then Kn , and the extrapolated intercept at $C_s/C_e = 0$ is $C_s = n$. Of course, for

linear isotherms, $n \gg C_0$, $C_s/C_0 = Kn$ is a constant, and n cannot be evaluated. Although Scatchard analysis has been applied infrequently in environmental chemistry outside a few metal and organic cation binding studies (Narine and Guy 1982, Stevenson 1982), it seems to be very useful in analyzing data now treated empirically. For example, the limiting free energy ($C_s = 0$) can readily be obtained from the Scatchard (or Langmuir) K and the equation

$$\Delta G = -RT \ln K \quad (4)$$

where ΔG = free energy
 R = gas constant
 T = absolute temperature.

Scatchard plots could also be used to evaluate the average free energy of sorption as a function of surface coverage, which is not straightforward using the Freundlich equation.

Gibbs

This is a theoretical isotherm seldom used in practice because of the difficulty in evaluating its parameters. It attempts to describe equilibrium in terms of the required changes in surface concentration (Voice and Weber 1983):

$$\Gamma_i = - \frac{a_i}{RT} \frac{d\gamma}{da_i} \quad (5)$$

where Γ_i = surface excess of component i (over that in the bulk phase)

a_i = activity of i

γ = surface tension.

Linear

All sorption isotherms probably reduce to this form in the case of limited surface coverage where sorption energetics are practically constant:

$$C_s = K C_0 \quad (6)$$

where C_s , C_0 , and K are defined as before. This equation is more commonly applicable to liquid-liquid partitioning than to surface interactions, but it also frequently is used for hydrophobic organics on soil and mineral surfaces (Pierce et al. 1974, Chiou et al. 1979, Karickhoff et al. 1979, Means et al. 1980, Briggs 1981, Schwarzenbach and Westall 1981, Horzempa and DiToro 1983, Weber et al. 1983). Thermodynamic equilibrium constants and thus ΔG cannot be determined directly from K without estimating the surface area

involved in sorption and the molecular surface area of the contaminant of interest.

Polynomial

This was suggested as an alternative to the Freundlich isotherm for empirical representation of data (Lambert 1967). No theoretical significance is assumed. The equation is

$$C_s = a C_0 + b C_0^2 + c C_0^3 + \dots \text{etc.} \quad (7)$$

where a , b and c are constants.

RESULTS AND DISCUSSION

TNT

Mathematical analysis

Sorption isotherms were obtained on the two commercial gels in well water alone and well water in admixture with distilled water and dilute electrolyte solutions. The isotherms were plotted as C_s vs C_0 , where these are the sorbed and equilibrium solution concentration in mg/kg and mg/L, respectively. All isotherms curved at low concentration (Fig. A1-A13), which precludes the use of a single equilibrium constant for predictive purposes.

I attempted to fit the data using Langmuir, Freundlich and polynomial equations. None of these approaches were highly successful in fitting the data. Even the Freundlich equation, which is the least sensitive, showed distinct nonlinearity. Visual inspection of the C_s vs C_0 curves suggested that a combination of Langmuir and linear sorption might explain the experimental curves.

The Scatchard linearization technique has been used regularly in biology and medicine to resolve two and more classes of independent binding sites (Rosenthal 1967, Feldman 1972, Munson and Rodbard 1980). Although it has not been used to analyze sorption of neutral organics in soils, it has been used to describe protein-binding of neutral chemicals. There appears to be no theoretical or practical impediment to its use, perhaps only the semantic one of calling the process binding in one case and sorption in the other. Since I can perceive no real difference between binding and sorption, I adopted this method of separating each sorption isotherm into components.

A smooth curve was first drawn through each set of points. Data were taken from the curve at appropriate intervals and replotted as C_s/C_0 vs C_0 . It was apparent that two distinct classes of binding

were required to explain the data. Scatchard parameters for Class 1 binding were estimated from the plots by drawing a straight line through the first few points and extrapolating to both axes. Class 2 binding was characterized by a large number of sites, and data were not taken at a high enough concentration to permit extrapolation of the second curve to the x-axis. The binding parameter was for practical purposes constant, so a line approximating the limiting sorption coefficient was drawn parallel to the x-axis. Three binding parameters were then defined by the plot: K_1 , n_1 , and K_2 , n_2 . After eq 3 is rearranged and the linear term added, the sorption equation takes the form

$$C_s = \frac{K_1 n_1 C_e}{1 + K_1 C_e} + K_2 n_2 C_e \quad (8)$$

The original data (Tables A1-A13) were then subjected to a nonlinear least-squares curve-fitting routine [flexible simplex method; see Himmelblau (1970) for a listing] and the best values of the three constants determined. The data are shown in Tables A3-A13 (Fig. A3-A13). For the first two sets, data were not taken at a high enough concentration to permit an accurate analysis by this method. The best-fit Scatchard parameters are shown in Table 1. In general the model fits the data quite well, as can be seen by comparing the measured and predicted concentrations in Tables A3-A13.

Effect of pH and ionic strength

Picking clear trends from the data in Table 1 is difficult. Interpretation is complicated by the inadvertent alteration of the pH when the ionic strength was changed. Also, the statistical uncertainty associated with the experimental procedure cannot be determined from these limited data. The addition of NaCl to Quik-Gel apparently reduced the equilibrium constant (K_1) by an order of magnitude and the sorptive strength of Class 1 sites (K_1 , n_1) by a factor of 5.3. It seems unlikely that the relatively small change in ionic strength per se produced by the addition of 0.05 M NaCl could have effected this large a change. However, the pH was reduced concomitantly by 0.65 units, a 4.5-fold change in hydrogen ion concentration, which suggests that loss of sorptivity and lowering of pH may be related. For Aqua-Gel the pH drop was only 0.25, or a 1.8-fold change in hydrogen ion concentration, while K_1 , n_1 , changed by a factor of only 1.2. The pH change accompanying addition of 0.05 M NaCl is in the wrong direction and too large to be accounted for by the expected change in the hydrogen ion activity coefficient. For a 0.05 M NaCl solution the measured pH should increase by the log of the activity coefficient (0.86), or 0.07 pH units (Butler 1964, chapter 12).

It may be that exchangeable H is being replaced by Na, causing both the reduction in pH and the loss of H-bonding capacity. DellaGuardia and Thomas (1983) also reported reduced sorption of

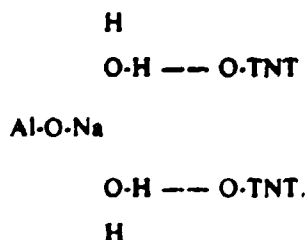
Table 1. Least-squares estimates of equilibrium constants for TNT on bentonite drilling muds.

Sorbent	Bentonite concentration (mg/6 mL)	Solution	I (mol/L)	T (°C)	pH	n_1 (mg/mg)	K_1 (L/mg)	K_2 (L/kg)	$-\Delta G_1$ (kcal/mol)
QO*	400	WW	0.0168	10	8.8	n.d.	n.d.	n.d.	n.d.
QO	200	WW	0.0168	11.5	n.d.	n.d.	n.d.	n.d.	n.d.
QO	100	WW	0.0168	10	8.1	46.7	3.53	21.7	9.90
QO	50	WW	0.0168	12	8.0	32.8	3.17	22.5	9.84
QO	composite†					40.0	2.49	22.1	9.71
QO	100	WW + NaCl	0.0455	10	7.35	94.8	0.332	16.2	8.57
QO	100	WW + DW	0.0028	10	9.0	50.6	2.01	18.3	9.59
QO	100	WW	0.0168	24	n.d.	41.2	1.49	22.4	9.88
AO	100	WW	0.0168	10	8.45	42.6	4.18	32.7	10.00
AO	50	WW	0.0168	10	n.d.	24.3	11.9	39.9	10.59
AO	composite					27.9	9.66	37.8	10.47
AO	100	WW + MgCl ₂	0.12	10	7.8	28.9	5.44	33.3	10.15
AO	100	WW + NaCl	0.0455	10	8.2	46.4	1.14	30.8	9.84
AO	100	WW + DW	0.0028	10	9.0	36.5	4.94	33.2	10.89
WB	100	WW	0.0168	10	8.8	23.0	0.830	15.9	9.09

* QO: Quik-Gel; AO: Aqua-Gel; WB: Wyoming bentonite; WW: well water; DW: distilled water; n.d.: not determined.

† Combined data from preceding four WW isotherms for QO and two WW isotherms for AO.

nitrobenzene on montmorillonite in the presence of dilute KCl. Small additions of neutral salts to montmorillonite suspensions are also known to decrease interparticle association, primarily by reducing face-edge association (deflocculation, (VanOlphen 1977)). Replacement of H by Na on Al-O-H and Fe-O-H edge groups might conceivably be responsible for all of these phenomena. This would explain the drastically reduced sorption energy of Class 1 sites (K_1 , ΔG_1), since Na associated with edge exchange sites would cause less efficient H bonding through coordinated water molecules in its hydration shell, e.g.



This mechanism could also explain the apparent increase in number of specific sites (n_1).

This is different from the explanation given for sorption of nitrobenzene (DellaGuardia and Thomas 1983), which was thought to be hydrogen bonded to water coordinated by exchange cations. This is probably not the mechanism for the Class 1 sorption of TNT on bentonite observed here, because the number of sites (n_1) is much lower than the ion exchange capacity for montmorillonite and because this mechanism doesn't explain the salt effect. The ion exchange capacity of montmorillonite is roughly 1 eq/kg, whereas the composite n_1 for Quik-Gel was 40 mg/kg, or 1.76×10^{-4} eq/kg. It may be that Class 2 sorption actually corresponds to sorption on exchange cations, but this remains a question since the capacity of these sites (n_2) cannot be determined from our data.

The slight decrease in nonspecific sorption (K_2) in dilute NaCl, if real, is also not likely to be caused directly by the increased ionic strength, since the hydrophobic effect should increase sorption by Class 2 sites if anything (see *Introduction*). Again, changes in interparticle association from face-edge to face-face may effectively compete for the available surface, decreasing TNT sorption. Because of its high capacity, nonspecific (Class 2) sorption is probably more closely related to the surface area of crystal faces than to that of edges. The addition of dilute NaCl to clay suspensions is known to bring about greater face-face (van der Waals) as-

sociation by reducing natural double-layer repulsion [aggregation, VanOlphen (1977)].

The average equilibrium constant (K_1) and free energy of sorption ($-\Delta G_1$) were higher for Aqua-Gel than for Quik-Gel. However, the average number of specific sites was lower for Aqua-Gel than for Quik-Gel. The average nonspecific sorption (K_2) was also higher for Aqua-Gel. Wyoming bentonite was lower in all three sorption parameters than the commercial muds. I can only speculate as to the reason for differences among the gels, as the manufacturer's literature (Appendix E) gives few clues. Quik-Gel contains a small quantity of organic polymeric additive, which may be in part responsible for its properties. Physical interactions in clay gel systems, especially in the presence of organic additives, are complicated and not well understood (VanOlphen 1977). Differences in surface area among the clays may be responsible for the small differences in nonspecific adsorption (K_2).

Effect of solids concentration

Although one of my stated objectives was to determine if solids concentration affected adsorption equilibria, I was not able to do this because the difference method of measuring sorbed concentrations does not lend itself to isotherm measurements over a wide range of solids concentration. This is because the changes in equilibrium concentration become too small to measure accurately at low solids concentrations. At high solids concentrations the differences are large but the measurements are less accurate because of the low concentrations. To measure differences in equilibrium constants over a narrow range of solids concentration by this method would require greater replication in order to increase and measure the precision, which was not done. Direct measurement of sorbed concentrations, preferably with radioisotopically labeled analytes, could be used to evaluate sorption at low solids concentrations.

Desorption

Transport calculations based on sorption "equilibrium" constants are only valid if sorption is completely reversible. Desorption isotherms were determined on two of the samples after overnight equilibration (Fig. A14 and A15; Tables A14 and A15). No hysteresis was observed, although in one case (Fig. A14) the desorption solution (well water) was inadvertently different from the sorption solution (0.05 M NaCl) so the exact shape of the isotherm was not reproduced. These experi-

ments were carried out within 24 hours. Sikka et al. (1980) and Spanggard et al. (1980) noted irreversible sorption of TNT after longer contact times with sediments. These types of loss are more likely to be associated with high-organic, nonsterile soils and sediments than with clay minerals. Although assessing the long-term stability of these systems was beyond the scope of this work, it is important from a monitoring and hazard-assessment perspective and ultimately for realistic transport modeling.

Sorption mechanism and thermodynamics

From the Scatchard analysis I have identified two types of sorption occurring simultaneously. Free energies of sorption ΔG were calculated for Class 1 sites by eq 4 after conversion of K_1 to mole fraction form (Table 1). The values are between -9 and -11 kcal/mol and are higher for Aqua-Gel than for Quik-Gel. These ΔG values suggest moderately strong bond formation between TNT and the gels. However, the free energy for the reaction is the sum of heat and entropy terms; according to the tenets of thermodynamics:

$$\Delta G = \Delta H - T \Delta S \quad (9)$$

where ΔH is the net energy of bond formation and ΔS is the change in entropy. The transfer of hydrophobic organics from an aqueous to a nonaqueous environment is generally accompanied by a considerable increase in entropy. Therefore, ΔH was expected to be less than ΔG . We can estimate ΔH from two of the samples, which were run at 10° and 24 °C, respectively (Tables A3 and A7), using the following equation (Pierce et al. 1974, Gerstl and Mingelgrin 1979):

$$-\Delta H = \frac{(\ln K_{T_1} - \ln K_{T_2})R}{(1/T_1) - (1/T_2)} \quad (10)$$

Substitution of the appropriate data from Table 1 gives a calculated ΔH of -10,290 cal/mol and entropy of -1.38 cal/mol K. The slight apparent loss of entropy is consistent with a strong bonding interaction.

For Class 2 sites, on the other hand, the K_1 values were nearly the same at the two temperatures ($\Delta H = 380$ cal/mol). Small positive enthalpies of transfer from water to an organic phase are not uncommon in hydrophobic interactions (Leo et al. 1971, Chiou et al. 1979, Tanford 1980). In any case the term is small and probably not significantly different from zero. Calculation of the free energy change for Class 2 sorption is not as straightforward

as for Class 1 sites, since n_1 is very large and cannot be estimated from our data. We can estimate a ΔG if we assume that monolayer coverage is the maximum capacity of the sorbent. The surface area occupied by a TNT molecule can be calculated from (Bansal et al. 1982):

$$A = 1.091 \times 10^{-16} [M \times 10^{24}/N]^{\frac{1}{2}} \quad (11)$$

where A is the area in cm^2 , M is the molecular weight of TNT, and N is Avogadro's Number. This gives a molecular area for TNT of $5.7 \times 10^{-15} \text{ cm}^2$, or 57 \AA^2 . The appropriate surface area for the sorbent is also in question, since we don't know if TNT penetrates the interlayer region. Assuming it does not, we use the external surface area of montmorillonite, which is roughly $20 \text{ m}^2/\text{g}$ (Lee et al. 1979). Therefore, monolayer coverage is estimated to be $20/57 \times 10^{-19} \times N = 5.8 \times 10^{-3} \text{ mol/g}$, or $1.3 \times 10^{-3} \text{ g TNT/g sorbent}$. In mole fraction form K_1 is 2.10×10^4 , ΔG is -5600 cal/mol, and ΔS is about 20 cal/mol K.

In spite of the assumptions involved, the calculation yields values for ΔG and ΔS that are quite typical of hydrophobic bonding interactions (Leo et al. 1971, Arakawa 1979, Tanford 1980, Goffredi and Liveri 1981). Thus, the data are consistent with the suggestions and indirect evidence of hydrogen bonding and hydrophobic bonding given earlier in this report. Electrostatic or charge-transfer interactions between the (negative) clay plates and electron-deficient aromatic rings may occur because their flat conformations facilitate close approach. This interaction would probably also enhance hydrogen bonding through the nitro groups and might explain the relatively large ΔH (≈ 10 kcal/mol) for Class 1 sorption. The data of Sikka et al. (1980) suggest a dual sorption mechanism for TNT on sediments as well, although they fit their data with a Freundlich isotherm. Using eq 8, I calculate interaction energies that are similar to those for bentonite.

DNT

Sorption of DNT appears to be similar to that of TNT, and the same model was used to fit the data. The results are summarized in Table 2; the complete results are given in Appendix B. The same trends were evident here, best seen by comparing the composite data for well water: n_1 was greater for Quik-Gel, and K_1 and K_2 were greater for Aqua-Gel. Apparent differences in the number of specific sites (n_1) between TNT and DNT may or may not be real. Composite K_1 values were slightly lower for DNT. Free energies of Class 1

Table 2. Least-squares estimates of equilibrium constants for DNT on bentonite drilling muds.

Sorbent	Bentonite concentration (mg/6 mL)	n_1 (mg/kg)	K_1 (L/mg)	K_2 (L/kg)	$-\Delta G_1$ (kcal/mol)
QG*	100	41.8	1.69	15.6	9.36
QG	200	37.9	1.84	16.0	9.41
QG	composite	35.2	1.98	17.8	9.45
AG	100	17.9	8.01	30.7	10.24
AG	200	15.6	13.7	33.0	10.54
AG	composite	17.0	10.6	31.3	10.40

* QG: Quik-Gel; AG: Aqua-Gel. All solutions were unamended well water ($I = 0.0168$), and the equilibration temperature was 10°C.

sorption were also nearly equal. These observations suggest that DNT and TNT are sorbed by the same mechanisms and that there is very little to distinguish between them energetically, in keeping with their very similar structures. Thus the data for DNT fit the same model of hydrogen bonding and hydrophobic sorption suggested for TNT. No hysteresis was observed on desorption for 2 hours after overnight equilibration (Fig. B4 and B6). Brodman et al. (1982) reported hydrogen bonding of DNT to free hydroxyls in nitrocellulose.

In some preliminary experiments in which all four analytes were added concurrently to drilling mud suspensions, DNT distribution coefficients decreased with time, while TNT distribution coefficients increased. This suggests that TNT can compete effectively with DNT for sorption sites and further confirms that the two have similar sorption mechanisms. The implication for groundwater analysis is that sorption effects may not be predictable from single-component isotherms only. For example, in the presence of larger amounts of TNT (a situation that is quite likely since DNT is usually only a minor contaminant in manufactured TNT), DNT sorption will be overestimated by the single-component isotherms presented here.

RDX and HMX

Sorption isotherms of RDX and HMX were run simultaneously using the HMX impurity peak in RDX. The results are given in Appendices C and D. Unlike those of TNT and DNT the isotherms appear to be linear and were fit to a linear model. Sikka et al. (1980) obtained similar results for RDX on sediments. Isotherms for two-hour sorption and desorption were reversible (Fig. C5 and D2). Sorption coefficients are summarized in Table 3.

Table 3. Least-squares estimates of equilibrium constants for RDX and HMX on bentonite drilling muds.

Compound	Sorbent	Concentration (mg/6 mL)	K (L/kg)
RDX	AG*	200	6.75
RDX	AG	400	6.39
RDX	QG	200	4.92
RDX	QG	400	5.79
RDX	AG	composite	6.62
RDX	QG	composite	5.77
HMX	AG	composite	8.87
HMX	QG	composite	13.25

* AG: Aqua-Gel; QG: Quik-Gel. All solutions were unamended well water ($I = 0.0168$), and the equilibration temperature was 10°C.

Although the simultaneous processing of HMX with RDX was inadvertent due to its presence as an impurity in the RDX used, it was fortuitous as I did not have enough pure HMX at the time to prepare a stock solution for isotherm measurements. Simultaneous measurements for these compounds can also be justified on both theoretical and practical grounds. Since the isotherms are linear over this range, the capacity of the clay is high relative to the amount being adsorbed; thus there should be no competition for active sites, and the compounds should behave independently. Although some HMX is manufactured, it is usually associated with RDX manufacture and will be detected only when RDX is present in significant amounts, so it is reasonable to study the two together.

The linear sorption coefficients are similar for RDX and HMX. There may be a slightly higher K for RDX on Aqua-Gel than on Quik-Gel, as was observed for Class 2 sorption of TNT and DNT. For HMX the preference seemed to be reversed,

but the difference may not be significant at these low concentrations. As will be discussed later the sorption mechanism for RDX and HMX apparently is not entirely entropic but involves the nitro groups in some way. Sikka et al. (1980) also found linear sorption for RDX on some sediments, and the sorption was similar in strength (K) to that found for the bentonites. The temperature dependence of sorption for RDX and HMX was not determined but is expected to be minor over the range of environmental interest.

Effect of drilling muds on analysis

The effect of Quik-Gel and Aqua-Gel on explosive contaminant measurements in groundwater can be computed using eq 8 in the case of TNT and DNT and eq 6 in the case of RDX and HMX. Since there were no apparent differences other than drilling mud type, it appeared justifiable to develop composite Scatchard parameters for each type. All the data for unamended well water were combined for each gel, and two composite, best-fit curves were obtained by computer curve-fitting for each analyte (Tables 1-3, Fig. A1, A2, B7, B8, C6, C7, D1, D3).

For example, suppose we want to know what concentration of drilling mud would cause the measured concentration of TNT to be 5% less than the true concentration. The mass balance equation is

$$C_i W = C_i V - C_e V \quad (12)$$

where W is the mass of bentonite in kilograms and V is the volume of equilibrating solution. C_i , C_e , and C_s are the initial, sorbed and equilibrium concentrations, respectively. For a 5% reduction in TNT concentration, we substitute $0.95C_s$ for C_e and solve for W/V :

$$C_i W = C_i V - 0.95 C_s V = 0.05 C_s V \quad (13)$$

$$W/V = \frac{0.05 C_s}{C_i} \quad (14)$$

Next, we solve eq 12 after substituting $0.95C_s$ for C_e and the appropriate Scatchard parameters. We also have to specify a value of C_i . For example, if we want to know how much Aqua-Gel would be required to cause a 5% reduction in the measured concentration when the true concentration (C_s) is 0.05 mg/L , the calculation would be:

$$C_i = \frac{(27.9)(9.66)(0.95)(0.5)}{1 + [(9.66)(0.95)(0.05)]} + 37.8(0.95)(0.05)$$

$$= 10.6 \text{ mg/kg}$$

and

$$W/V = \frac{(0.05)(0.05)}{10.6} = 0.00024 \text{ kg/L.}$$

That is, $240 \text{ mg Aqua-Gel/L}$ is required to cause a 5% error in the analysis at the 0.05-mg/L level. Because the isotherms are curved, different concentration values will be affected differently by the same bentonite concentration. The effect will be less at higher concentrations. For example, at the 1-mg/L level, $820 \text{ mg Aqua-Gel/L}$ are required to cause a 5% error. Analyses will be less sensitive to Quik-Gel than to Aqua-Gel. A 5% loss at the 0.05-mg/L level would require $470 \text{ mg Quik-Gel/L}$. Analysis error for any other combination of analyte, concentration and level of interference can be calculated similarly.

SEM and EDXA analysis of bentonite wells

Samples of well water from Tooele Army Depot, Utah, (#008) and from Milan Army Ammunition Plant, Tennessee, (#N3B) were obtained for examination by scanning electron microscope (SEM) and energy dispersive X-ray analysis (EDXA). These wells were drilled with bentonite muds, and it was of interest to see if residual bentonite particles could be found in the water and if so, to estimate their concentration.

Considerable turbidity and settleable solids were visible in both samples. However, after removal of soluble salts, less than 1% of the suspended particles in either sample was identified as bentonite by SEM and EDXA. Samples were also examined without removal of soluble salts; the salt particles remaining after removal of water far outnumbered the bentonite on a mass basis. These semi-quantitative observations and the calculations in the previous section suggest that analytically significant concentrations of bentonite are not present in these well waters.

Moreover, it was not possible to conclude that the bentonite particles observed were derived from drilling muds. Examination of Aqua-Gel and Quik-Gel particles by SEM and EDXA in comparison with reference Wyoming bentonite failed to

differentiate among them. Thus, even the small number of bentonite particles found in the well water could have come from the natural aquifer material.

Other studies

Octanol-water partition coefficients

As indicated in the *Introduction*, octanol-water partition coefficients are frequently correlated with sorption coefficients, particularly for soils and sediments containing organic matter. When sorption coefficients are normalized to organic carbon or organic matter content, the correlation equation can be used to predict sorption coefficients for new or untested chemicals simply from their octanol-water partition coefficients. Although this rationale frequently works well for natural soils, there was some question as to whether it would hold for polar surfaces such as clay minerals and polar solutes such as TNT. Here specific interactions may significantly increase the sorption, as they do for soils of low organic carbon content (Means et al. 1982).

Table 4 lists the octanol-water partition coefficients determined in this study along with values from the literature where available. The composite K' values for the nonspecific sorption component of the four contaminants are also presented. Curiously the sorption coefficients for TNT and RDX are quite similar to their K_{ow} s. For DNT they are lower and for HMX higher, suggesting a relationship between K/K_{ow} and the number of nitro groups per molecule. Thus, the octanol-water analogy fails to explain completely even the linear sorption component of these four compounds on bentonite. The K/K_{ow} ratio suggests specific sorption due to the nitro group. The correspondence for TNT and RDX may be purely accidental.

Water solubilities

Water solubilities are also sometimes used to estimate sorption coefficients (Chiou et al. 1979, Karickhoff 1981), although the correlation is generally inferior to octanol-water for solids, even with melting point correction. The reliability of literature data for explosive contaminants is not known, and it seemed desirable to make a new set of measurements under uniform conditions (Table 5). The measured solubilities for TNT and RDX are in good agreement with literature values. The large discrepancy for DNT is unexplained. The literature value cited by Spanggard et al. (1980b) was from a 1925 publication. Our value could be low if equilibrium was not reached or if DNT was

Table 4. Octanol-water partition coefficients and equilibrium constants of explosive contaminants at $23^\circ \pm 2^\circ\text{C}$.

Compound	$\log K_{ow}^*$		$\log K^\dagger$	
	This study	From literature	Aqua-Gel	Quik-Gel
TNT	1.65	n.a.	1.57	1.34
DNT	1.88	1.98**	1.50	1.25
RDX	0.88	0.87††	0.82	0.76
HMX	0.14	n.a.	0.95	1.12

* In the conventional volume/volume units (L water/L octanol).

† In L/kg K is K' for TNT and DNT.

** From Hansch and Leo (1979).

†† From Sikka et al. (1980).

Table 5. Water solubilities of explosive contaminants (mg/L).

Compound	S^* (mg/L)	S (from literature)† (mg/L)
TNT	137	130, 117 (20°C)
DNT	185	273 (22°C)
RDX	43.2	42.2 (20°C), 44.7 (18°C)
HMX	—	5.0 (22°C)

* Mean of two or three determinations done on different days. All were determined at $23^\circ \pm 2^\circ\text{C}$.

† TNT, DNT, RDX from Spanggard et al. (1980); HMX from Glover and Hoffsommer (1973).

sorbed onto the 0.1- μm polycarbonate filters used to prepare the saturated solution for analysis. I believe neither to be the case, as the same procedure was used for the other compounds. These filters were also used to prepare the aqueous phase for K_{ow} determinations reported here. I have recommended polycarbonate membranes for filtering water samples for explosives analyses (Jenkins et al. 1984). The solubility of HMX was not determined since I didn't have enough pure material.

The expected inverse correlations between water solubility and K_{ow} or soil K (Chiou et al. 1979) fail to explain the difference in sorptive or partitioning behavior. According to the model, RDX and HMX should have higher K_{ow} s than TNT and DNT, which is clearly not the case. Bannerjee et al. (1980) reported that the solubility model fails to predict the K_{ow} for RDX. Melting point correction significantly improved the prediction for RDX and HMX, but neither the corrected nor uncorrected model predicts the correct K_{ow} for TNT

Table 6. Predicted and measured octanol-water partition coefficients for explosive contaminants.

Compound	Calculated from solubility*		This study
	Uncorrected	Corrected	
TNT	2,040	669	44.7
DNT	1,430	594	75.9
RDX	4,400	25.7	7.59
HMX	23,180	13.6	1.38

* According to Banerjee et al. (1980).

and DNT or HMX by an order of magnitude (Table 6). While a relationship to K_{ow} may partially explain why the sorption of TNT and DNT is different from that of RDX and HMX, it fails to explain the difference between members within each pair, for which the expected order is reversed. The analogy of solubility to sorption better explains the order within pairs of like compounds. This information can be rationalized if we postulate that sorption is a function of both hydrophobicity and the number of nitro groups per molecule. Thus, within each pair the number of nitro groups dictates the magnitude of K . It probably makes sense that the number of nitro groups is also related to solubility, since both sorption and solubility are due to solute surface interactions (solubility can be considered the equilibrium state resulting from self-adsorption).

Actually it isn't necessary to invoke hydrophobic effects to explain sorption of these four compounds. The assumed order of Lewis acid strengths would be TNT > DNT > HMX > RDX, the same as the order of their K values on bentonite. Specific sorption of RDX and HMX on some organic polymers has been inferred on the basis of chromatographic data (Freeman et al. 1976)

SUMMARY

Sorption of TNT, DNT, RDX and HMX on two commercial bentonite drilling muds was shown. Equations were developed to describe their sorption from well water at 10°C as a function of analyte concentration. The equations were based on mechanistic models for sorption in which two sorption processes occur simultaneously. These can be described as specific and nonspecific. The specific type was operable only for TNT and DNT and was caused by a moderately high energy bond ($\Delta G \approx \Delta H \approx 10$ kcal/mol). This was attributed to

hydrogen bonding with edge or surface hydroxyls and/or to interaction between negatively charged clay plates and the aromatic ring and between positive edge groups and the electron pairs on the nitro groups forming a kind of sandwich between clay faces and edges. These interactions may be enhanced in aromatic molecules because of internal charge transfer and flat conformation. This was not observed with RDX and HMX, possibly because of steric effects and/or weaker internal charge transfer in the saturated ring. These compounds exhibited only nonspecific interactions, as exemplified by the linear sorption isotherms.

For TNT the nonspecific (linear) component of the isotherm appeared to be unaffected by increasing the temperature from 10° to 24°C. This is typical when sorption is dominated by the hydrophobic effect. In thermodynamic terms this means that sorption results from the increase in the system entropy when sorbed water molecules exchange with solute molecules. This doesn't mean that the sorption or desorption enthalpies are zero, only that their sum, or the net enthalpy for the exchange reaction, is essentially zero.

However, the nonspecific interaction could not be explained entirely by either the octanol-water partitioning or the solubilities of these compounds. The higher sorption coefficients of the aromatics, TNT and DNT, were expected from their higher K_{ow} s. However, within each pair the order is reversed, and the compound with the higher K_{ow} (and higher solubility) has the lower sorption coefficient. This suggests an effect due to the additional nitro group on TNT and HMX compared to DNT and RDX. This makes physical sense if nitro groups are also involved in nonspecific sorption including self-adsorption (solubility) of these compounds, if the enhanced Lewis acidity of the ring due to the additional nitro group is involved, or both. The greater Lewis acidity of the aromatics compared to the triazines may be the reason for their greater sorption as well, rather than strictly entropic effects. Finally, several mechanisms may be contributing to the nonspecific sorption component. The planar conformation of the aromatics is expected to enhance their sorption by van der Waals forces over that of the triazines, which tend to assume nonplanar chair and crown conformations (Freeman et al. 1976).

Sorption of TNT and DNT appear to be influenced by each other's presence and therefore probably by other contaminants in groundwater. This is thought to be due to competition for the few most-active sites on the mineral. Thus, extrapolation of single-species isotherms obtained in the

laboratory to predict sorption in the environment is risky and would in this case result in an overestimate of actual sorption. RDX and HMX sorption did not appear to be affected by the other's presence, probably because the extent of sorption is low and the sorption capacity is very high. Sorption parameters on bentonite were similar to those found for TNT and RDX on sediments, suggesting that the clay content of natural soils and sediments will materially affect sorption of these contaminants in the environment.

LITERATURE CITED

- APHA-AWWA-WPCF** (1980) *Standard Methods for the Examination of Water and Wastewater*. 15th Edition. American Public Health Association, American Water Works Association, Water Pollution Control Federation.
- Arakawa, K., K. Tokiwano, N. Ohtomo and H. Uedaira** (1979) A note on the nature of ionic hydration and hydrophobic interactions in aqueous solutions. *Bulletin of the Chemical Society of Japan*, 52(9): 2483-2488.
- Banerjee, S., S.H. Yalkowsky and S.C. Valvani** (1980) Water solubility and octanol/water partition coefficients of organics. Limitations of the solubility-partition coefficient correlation. *Environmental Science and Technology*, 14(10): 1227-1229.
- Bansal, O.P., M. Prasad and S.N. Srivastava** (1982) Adsorption of oxamyl on montmorillonites: A thermodynamic approach to the adsorption mechanism. *Agricultural and Biological Chemistry (Tokyo)*, 46(2): 323-332.
- Bowman, B.T.** (1981) Anomalies in the log Freundlich equation resulting in deviations in adsorption K values of pesticides and other organic compounds when the system of units is changed. *Journal of Environmental Science and Health B*, 16(2): 113-123.
- Briggs, G.G.** (1981) Theoretical and experimental relationships between soil adsorption, octanol-water partition coefficients, water solubilities, bioconcentration factors, and the parachor. *Journal of Agricultural and Food Chemistry*, 29: 1050-1059.
- Brodman, B.W., N. Lampner and J. Eng** (1982) Hydrogen bonding of dinitrotoluene isomers to unesterified hydroxyl groups in nitrocellulose. *Journal of Applied Polymer Science*, 27: 3621-3623.
- Butler, J.N.** (1964) *Ionic Equilibrium: A Mathematical Approach*. Reading, Massachusetts: Addison-Wesley.
- Chlou, C.T., L.J. Peters and V.H. Freed** (1979) A physical concept of soil-water equilibria for non-ionic organic compounds. *Science*, 206(16): 831-832.
- Chlou, C.T., P.E. Porter and D.W. Schmedding** (1983) Partition equilibria of nonionic organic compounds between soil organic matter and water. *Environmental Science and Technology*, 17(4): 227-231.
- Chou, S.F.J., R.A. Griffen and M.I.M. Chou** (1982) Effect of soluble salts and caustic soda on solubility and adsorption of hexachlorocyclopentadiene. *Proceedings, Eighth Annual Research Symposium of the Solid and Hazardous Waste Research Division*, Cincinnati, Ohio, 8-10 March. U.S. Environmental Protection Agency, Cincinnati, Ohio.
- Della Guardia, R.A. and J.K. Thomas** (1983) Photo-processes on colloidal clay systems: Tris (2,2'-bipyridinium) ruthenium II bound to colloidal kaolin and montmorillonite. *Journal of Physical Chemistry*, 87(6): 990-998.
- Dexter, R.N. and S.P. Pavlov** (1978) Distribution of stable organic molecules in the marine environment: Physical, chemical aspects. Chlorinated hydrocarbons. *Marine Chemistry*, 7: 67-84.
- DiToro, D.M. and L.M. Horzempa** (1982) Reversible and resistant components of PCB adsorption-desorption isotherms. *Environmental Science and Technology*, 16(9): 594-602.
- Dudgeon, C.R. and R.J. Cox** (1976) Drilling mud invasion of unconsolidated aquifer materials. Australian Water Resources Council Technical Paper No. 17, Australian Government Publishing Service, Canberra.
- Dudgeon, C.R. and P.S. Huyakorn** (1976) Effects of near-well permeability variations in well performance. Australian Water Resources Council Technical Paper No. 18, Australian Government Publishing Service, Canberra.
- Feldman, H.A.** (1972) Mathematical theory of complex ligand-binding systems at equilibrium: Some methods for parameter fitting. *Analytical Biochemistry*, 48: 317-338.
- Freeman, D.H. and L.S. Cheung** (1981) A gel partition model for organic desorption from a pond sediment. *Science*, 214: 790-792.
- Freeman, D.H., R.M. Angeles and I.C. Poinescu** (1976) High-performance liquid chromatographic separation of RDX and HMX explosives on adsorptive polymers. *Journal of Chromatography*, 118: 157-166.

- Fusi, P., G.G. Ristori and M. Franci (1982) Adsorption and catalytic decomposition of 4-nitrobenzenesulfonylmethylcarbamate by smectite. *Clays and Clay Minerals*, 30(4): 306-310.
- Gerstl, Z. and U. Mingelgrin (1979) A note on the adsorption of organic molecules on clays. *Clays and Clay Minerals*, 27(4): 285-290.
- Glover, D.J. and J.C. Hoffsommer (1973) Thin-layer chromatographic analysis of HMX in water. *Bulletin of Environmental Contamination and Toxicology*, 10(5): 302-304.
- Goffredi, M. and V.T. Liveri (1981) Thermodynamics of transfer of non-ionic solutes between immiscible liquid phases. I. Transfer of normal alcohols from n-octane to water at 25 °C. *Journal of Solution Chemistry*, 10(10): 693-698.
- Grauer, Z., S. Yariv, L. H. Kallai and D. Avnir (1983) Effect of temperature on the conformation of dibenzotropone adsorbed on montmorillonite. *Journal of Thermal Analysis*, 26: 49-64.
- Hale, V.W., T.B. Stanford and L.G. Taft (1979) Evaluation of the environmental fate of munitions in soil. Final report, Contract No. DAMD 17-76-C-6065, Battelle Columbus Laboratories, Columbus, Ohio.
- Hamaker, J.W. and J.M. Thompson (1972) Adsorption. In *Organic Chemicals in the Soil Environment* (C.A.I. Goring and J.W. Hamaker, Ed.). New York: Marcel Dekker, Inc. Vol. 1, Chap. 2, pp. 49-143.
- Hansch, C. and A. Leo (1979) *Substituent Constants for Correlation Analysis in Chemistry and Biology*. New York: John Wiley and Sons.
- Haque, R. and W.R. Coshov (1971) Adsorption of isocil and bromacil from aqueous solution on some mineral surfaces. *Environmental Science and Technology*, 5(2): 139-141.
- Himmelblau, D.M. (1970) *Process Analysis by Statistical Methods*. New York: John Wiley and Sons.
- Horzempa, L.M. and D.M. DiToro (1983) PCB partitioning in sediment water systems: The effect of sediment concentration. *Journal of Environmental Quality*, 12(3): 373-380.
- Jenkins, T.F., C.F. Bauer, D.C. Leggett and C.L. Grant (1984) Reverse phase HPLC method for analysis of TNT, RDX, HMX, and 2,4-DNT in munitions wastewater. USA Cold Regions Research and Engineering Laboratory, CRREL Report 84-29.
- Jensen, W.B. (1982) Lewis acid-base interactions and adhesion theory. *Rubber Chemistry and Technology*, 55(3): 881-901.
- Karickhoff, S.W. (1981) Semi-empirical estimation of sorption of hydrophobic pollutants on natural sediments and soils. *Chemosphere*, 10(8): 833-846.
- Karickhoff, S.W., D.S. Brown and T.A. Scott (1979) Sorption of hydrophobic pollutants on natural sediments. *Water Research*, 13: 241-248.
- Lambert, S.M. (1967) Functional relationship between sorption in soil and chemical structure. *Journal of Agricultural and Food Chemistry*, 15(4): 572-576.
- Lee, M.C., R.A. Griffen, M.L. Miller and E.S.K. Chian (1979) Adsorption of water-soluble polychlorinated biphenyl arochlor 1242 and used capacitor fluid by soil materials and coal chars. *Journal of Environmental Science and Health*, A14(5): 415-442.
- Leermakers, P.A., H.T. Thomas, L.D. Wels and F.C. James (1966) Spectra and photochemistry of molecules adsorbed on silica gel. IV. *Journal of the American Chemical Society*, 88(22): 5075-5083.
- Leo, A., C. Hansch and D. Elkins (1971) Partition coefficients and their use. *Chemical Reviews*, 71(6): 525-554.
- Lewis, G.N. and G.T. Seaborg (1940) The acidity of aromatic nitro compounds toward amines. The effect of double chelation. *Journal of the American Chemical Society*, 62: 2122-2126.
- Means, J.C., S.G. Wood, J.J. Hassett and W.L. Banwart (1980) Sorption of polynuclear aromatic hydrocarbons by sediments and soils. *Environmental Science and Technology*, 14(12): 1524-1528.
- Means, J.C., S.G. Wood, J.J. Hassett and W.L. Banwart (1982) Sorption of amino- and carboxy-substituted polynuclear aromatic hydrocarbons by sediments and soils. *Environmental Science and Technology*, 16(2): 93-98.
- Meyers, P.A. and T.G. Oas (1978) Comparison of association of different hydrocarbons with clay particles in simulated seawater. *Environmental Science and Technology*, 12(8): 934-937.
- Mingelgrin, U. and Z. Gerstl (1983) Reevaluation of partitioning as a mechanism of nonionic chemicals adsorption in soils. *Journal of Environmental Quality*, 12(1): 1-11.
- Mortland, M.M. (1970) Clay-organic complexes and interactions. *Advances in Agronomy*, 22: 75-117.
- Munson, P.J. and D. Rodbard (1980) LIGAND: A versatile computerized approach for characterization of ligand-binding systems. *Analytical Biochemistry*, 107: 220-239.
- Narine, D.R. and R.D. Guy (1982) Binding of diquat and paraquat to humic acid in aquatic environments. *Soil Science*, 133(6): 356-363.

- O'Connor, D.J. and J.P. Connolly (1982) The effect of concentration of adsorbing solids on the partition coefficient. *Water Research*, 14: 1517-1523.
- Parfitt, R.L. and M.M. Mortland. (1968) Ketone adsorption on montmorillonite. *Soil Science Society of America Proceedings*, 32(3): 355-363.
- Pierce, R.H., C.E. Olney and G.T. Felbeck (1974) pp'-DDT adsorption to suspended particulate matter in seawater. *Geochimica et Cosmochimica Acta*, 38: 1061-1073.
- Rosenthal, H.E. (1967) A graphic method for the determination of binding parameters in a complex system. *Analytical Biochemistry*, 20: 525-532.
- Scatchard, G. (1949) The attractions of proteins for small molecules and ions. *Annals of the New York Academy of Sciences*, 51: 660-672.
- Schwarzenbach, R.P. and J. Westall (1981) Transport of nonpolar organic compounds from surface water to groundwater. Laboratory sorption studies. *Environmental Science and Technology*, 15 (11): 1360-1367.
- Sikka, H.C., S. Banerjee, E.T. Pack and H.T. Appleton (1980) Environmental fate of RDX and TNT. Final report, Contract No. DAMD 17-77-C-7026, Syracuse Research Corporation, Syracuse, New York.
- Solomon, D.H. (1968) Clay minerals as electron acceptors and/or electron donors in organic reactions. *Clays and Clay Minerals*, 16: 31-39.
- Spanggord, R.J., T. Mill, T.-W. Chou, W.R. Mabey, J.H. Smith and S. Lee (1980a) Environmental fate studies on certain munition wastewater constituents. Final report, Phase I—Literature review. Contract No. DAMD 17-78-C-8081, SRI International, Menlo Park, California.
- Spanggord, R.J., T. Mill, T.-W. Chou, W.R. Mabey, J.H. Smith and S. Lee (1980b) Environmental fate studies on certain munition wastewater constituents. Final report, Contract No. DAMD 17-78-C-8081, SRI International, Menlo Park, California.
- Stevenson, F.J. (1982) *Humus Chemistry, Genesis, Composition, Reactions*. New York: John Wiley and Sons, pp. 367-370.
- Sullivan, K.F., E.L. Atlas and C.-S. Glam (1982) Adsorption of phthalic esters from seawater. *Environmental Science and Technology*, 16(7): 428-432.
- Tanford, C. (1980) *The Hydrophobic Effect: Formation of Micelles and Biological Membranes*. Second Edition. New York: John Wiley and Sons.
- Terrier, F. (1982) Rate and equilibrium studies in Jackson-Meisenheimer complexes. *Chemical Reviews*, 82(2): 77-152.
- THAMA (1980) Adsorptive properties of Quik-Gel. Memorandum for record, USA Toxic and Hazardous Materials Agency, Aberdeen Proving Ground, Maryland.
- THAMA (1982) Sampling and chemical analysis quality assurance program. USA Toxic and Hazardous Materials Agency, Aberdeen Proving Ground, Maryland.
- THAMA (1983) Geotechnical requirements for drilling, monitor wells, data acquisition, and reports. USA Toxic and Hazardous Materials Agency, Aberdeen Proving Ground, Maryland.
- Theng, B.K.G. (1974) *The Chemistry of Clay-Organic Reactions*. New York: John Wiley and Sons.
- Van Olphen, H. (1977) *An Introduction to Clay Colloid Chemistry*. Second Edition. New York: John Wiley and Sons.
- Voice, T.C. and W.J. Weber (1983) Sorption of hydrophobic compounds by sediments, soils, and suspended soils. I. Theory and background. *Water Research*, 17(10): 1433-1441.
- Voice, T.C., C.P. Rice and W.J. Weber (1983) Effect of solids concentration on the sorptive partitioning of hydrophobic pollutants in aquatic systems. *Environmental Science and Technology*, 17(9): 513-518.
- Wauchope, R.D. and W.C. Koskinen (1983) Adsorption-desorption equilibria of herbicides in soil: A thermodynamic perspective. *Weed Science*, 31: 504-512.
- Weber, W.J., T.C. Voice, M. Pirbazzari, G.E. Hunt and D.M. Ulanoff (1983) Sorption of hydrophobic compounds by sediments, soils, and suspended solids. II. Sorbent evaluation studies. *Water Research*, 17(10): 1443-1452.
- Wildish, D.J., C.D. Metcalf, H.M. Akagi and D.W. McLeese (1980) Flux of arochlor 1254 between estuarine sediments and water. *Bulletin of Environmental Contamination and Toxicology*, 24: 20-26.
- Yariv, S., J.D. Russell and V.C. Farmer (1966) Infrared study of the adsorption of benzoic acid and nitrobenzene in montmorillonite. *Israel Journal of Chemistry*, 4: 201-213.
- Yurow, H.W. and P.A. Tarantino (1980) Adsorption of various compounds from aqueous solution on Quik-Gel (bentonite). Unpublished technical report, Chemical Systems Laboratory, Aberdeen Proving Ground, Maryland.

APPENDIX A: RESULTS FOR TNT

Table A1. TNT sorption on Quik-Gel (400 mg/6 mL; 10°C; pH 8.8).

Solution (mg/L)		Solid (mg/kg)	
Initial	Equilibrium		
C_i	C_e	C_s	C_s (predicted)*
9.45	2.92	101.0	99.6
3.78	0.754	45.5	42.7
3.78	0.754	45.5	42.7
1.51	0.228	19.2	19.5
1.51	0.238	19.0	20.1
0.605	0.124	7.30	12.2
0.605	0.101	7.65	10.3
0.242	0.0366	3.06	4.15
0.0967	0.0137	1.24	1.62

*From eq 8: $C_s = \frac{99.56C_e}{1+2.489C_e} + 22.07C_e$

Table A2. TNT sorption on Quik-Gel (200 mg/6 mL; 11.5°C).

Solution (mg/L)		Solid (mg/kg)	
Initial	Equilibrium		
C_i	C_e	C_s	C_s (predicted)*
4.107	1.85	67.7	73.7
4.107	1.89	66.5	74.7
1.643	0.552	32.7	35.3
1.643	0.542	33.0	34.9
0.637	0.188	14.1	16.9
0.637	0.197	13.8	17.5
0.263	0.075	5.63	7.95
0.263	0.112	4.52	11.2
0.105	0.0340	2.13	3.87
0.1051	0.0255	2.39	2.95
0.0421	0.0336	0.254	3.83
0.000	0.0000	0.000	0.00

*From eq 8: $C_s = \frac{99.56C_e}{1+2.489C_e} + 22.07C_e$

Table A3. TNT sorption on Quik-Gel (100 mg/6 mL; 10° ± 2°C; pH 8.1 ± 0.2).

Solution (mg/L)		Solid (mg/kg)	
Initial	Equilibrium		
C_i	C_e	C_s	C_s (predicted)*
9.16	6.15	174	178
9.16	6.03	181	176
3.66	2.19	89.0	89.0
3.66	2.22	87.2	89.7
1.47	0.660	47.8	47.1
1.47	0.658	47.9	47.0
0.586	0.174	24.0	21.6
0.586	0.174	24.0	21.6
0.234	0.0711	9.68	10.9
0.234	0.0750	9.44	11.4
0.0938	0.0345	3.68	5.83
0.0938	0.0364	3.56	6.12
0.0938	0.0331	3.76	5.61
0.0375	0.0129	1.43	2.32
0.0375	0.0152	1.30	2.71
0.0000	0.0000	0.00	0.00

*From eq 8: $C_s = \frac{105.0C_e}{1+3.331C_e} + 21.75C_e$

Table A4. TNT sorption on Quik-Gel (50 mg/6 mL; 12° ± 2°C; pH 8.0 ± 0.5).

Solution (mg/L)		Solid (mg/kg)	
Initial	Equilibrium		
C_i	C_e	C_s	C_s (predicted)*
9.45	7.60	206	203
9.45	7.65	201	204
3.78	2.94	94.2	95.8
3.78	2.94	94.2	95.8
1.51	1.08	49.8	49.7
1.51	1.06	52.1	49.2
0.605	0.367	26.0	25.9
0.605	0.365	26.2	25.8
0.242	0.136	11.9	13.0
0.242	0.136	11.9	13.0
0.242	0.128	12.8	12.4
0.0967	0.0520	5.21	5.82
0.0387	0.0213	1.87	2.56
0.0387	0.0209	1.92	2.51
0.0000	0.0000	0.00	0.00

*From eq 8: $C_s = \frac{104.2C_e}{1+3.170C_e} + 22.50C_e$

Table A5. TNT sorption on Quik-Gel (100 mg/6 mL; 10°C; pH 7.35; 0.05 M NaCl; $I = 0.0455$).

Solution (mg/L)		Solid (mg/kg)	
Initial C_i	Equilibrium C_e	C_s	C_s (predicted)*
9.123	6.32	166	167
9.123	6.30	167	166
3.649	2.32	79.4	78.9
3.649	2.33	78.5	79.1
1.460	0.871	36.0	35.4
0.5839	0.343	14.5	15.2
0.5839	0.345	14.4	15.3
0.5839	0.345	14.4	15.3
0.2336	0.124	6.49	5.76
0.2336	0.122	6.58	5.67
0.0943	0.0454	2.95	2.14
0.0943	0.0476	2.82	2.24
0.0374	0.0135	1.43	0.64
0.0000	0.0000	0.00	0.00

*From eq 8: $C_s = \frac{31.4C_e}{1 + 0.3316C_e} + 16.22C_e$.

Table A6. TNT sorption on Quik-Gel (100 mg/6 mL; 10°C; pH 9.0; well water/distilled water, 1:5; $I = 0.0028$).

Solution (mg/L)		Solid (mg/kg)	
Initial C_i	Equilibrium C_e	C_s	C_s (predicted)*
9.083	6.36	161	163
9.083	6.30	165	162
3.633	2.26	81.4	82.8
3.633	2.26	81.4	82.8
1.453	0.704	45.1	42.5
1.453	0.719	44.2	43.1
0.5812	0.226	21.4	20.0
0.5812	0.232	21.1	20.3
0.2325	0.105	7.72	10.7
0.2325	0.0965	8.23	10.0
0.0930	0.0334	3.52	3.80
0.0930	0.0417	3.07	4.68
0.0372	0.0201	1.02	2.33
0.0372	0.0288	0.501	3.30
0.0000	0.0000	0.000	0.00

*From eq 8: $C_s = \frac{101.8C_e}{1 + 2.014C_e} + 18.29C_e$.

Table A7. TNT sorption on Quik-Gel (100 mg/6 mL; 24°C).

Solution (mg/L)		Solid (mg/kg)	
Initial C_i	Equilibrium C_e	C_s	C_s (predicted)*
9.083	6.177	175.7	175
3.633	2.275	81.07	82.7
3.633	2.255	82.26	82.2
1.453	0.7556	41.72	38.7
0.5812	0.2864	17.49	18.7
0.5812	0.2794	17.91	18.3
0.2325	0.0978	8.047	7.41
0.0930	0.04643	2.823	3.70
0.0930	0.05397	2.366	4.27
0.0930	0.0345	3.548	2.78
0.0372	0.0207	0.983	1.69
0.0372	0.0274	0.582	2.23
0.0372	0.0130	1.448	1.07
0.0000	0.0000	0.000	0.00

*From eq 8: $C_s = \frac{61.24C_e}{1 + 1.486C_e} + 22.38C_e$.

Table A8. TNT sorption on Aqua-Gel (100 mg/6 mL; 10°C; pH 8.4-8.5).

Solution (mg/L)		Solid (mg/kg)	
Initial C_i	Equilibrium C_e	C_s	C_s (predicted)*
9.38	5.65	223	226
9.38	5.60	226	224
3.75	1.97	103	102
3.75	1.95	104	102
1.50	0.649	50.7	52.3
1.50	0.650	50.7	52.4
0.601	0.187	24.8	24.8
0.601	0.187	24.7	24.8
0.240	0.0499	11.3	8.99
0.0961	0.0171	4.73	3.40
0.0384	0.0075	1.79	1.54
0.0000	0.0000	0.00	0.00

*From eq 8: $C_s = \frac{178.0C_e}{1 + 4.180C_e} + 32.70C_e$.

Table A9. TNT sorption on Aqua-Gel (50 mg/6 mL; 10°C).

Solution (mg/L)		Solid (mg/kg)	
Initial	Equilibrium	C_s	C_s (predicted)*
C_i	C_e	C_s	C_s (predicted)*
9.273	6.936	299.5	301
9.273	6.927	300.7	300
3.709	2.551	127.5	125
1.484	0.9618	59.06	60.7
1.484	0.9474	60.69	60.1
0.5934	0.3187	31.62	32.0
0.5934	0.3203	31.44	32.0
0.2374	0.0912	16.40	16.3
0.2374	0.0928	16.22	16.5
0.0949	0.0291	8.14	7.42
0.0949	0.0315	7.84	7.89
0.0830	0.00884	3.57	2.67
0.0000	0.00000	0.00	0.00

*From eq 8: $C_s = \frac{289.5C_e}{1 + 11.91C_e} + 39.87C_e$

Table A10. TNT sorption on Aqua-Gel (100 mg/6 mL; 10°C; pH 7.8 ± 0.1; 0.047 M MgCl₂/well water, 5:1; $I \approx 0.12$).

Solution (mg/L)		Solid (mg/kg)	
Initial	Equilibrium	C_s	C_s (predicted)*
C_i	C_e	C_s	C_s (predicted)*
9.259	5.626	218	215
9.259	5.690	214	217
3.704	2.072	98.1	95.5
3.704	2.098	96.6	96.4
1.482	0.710	45.1	46.6
1.482	0.705	45.3	46.4
0.593	0.219	22.2	23.0
0.237	0.0572	10.3	8.76
0.0948	0.0175	4.61	3.09
0.0379	0.0068	1.90	1.26
0.0000	0.0000	0.00	0.00

*From eq 8: $C_s = \frac{157.0C_e}{1 + 5.439C_e} + 33.29C_e$

Table A11. TNT sorption on Aqua-Gel (100 mg/6 mL; 10°C; pH 8.2; 0.05 M NaCl; $I \approx 0.0455$).

Solution (mg/L)		Solid (mg/kg)	
Initial	Equilibrium	C_s	C_s (predicted)*
C_i	C_e	C_s	C_s (predicted)*
9.140	5.520	215	214
9.140	5.565	213	215
3.666	1.925	104	99.1
1.462	0.6410	49.0	50.7
1.462	0.6736	47.1	52.2
0.5849	0.1876	23.8	23.0
0.5849	0.1914	24.2	22.4
0.2340	0.0577	10.6	8.89
0.2340	0.0647	10.2	9.82
0.0936	0.0178	4.31	3.00
0.0374	0.0071	1.80	1.23
0.0000	0.0000	0.00	0.00

*From eq 8: $C_s = \frac{145.6C_e}{1 + 3.136C_e} + 30.78C_e$

Table A12. TNT sorption on Aqua-Gel (100 mg/6 mL; 10°C; pH 9.0; well water/distilled water, 1:5; $I \approx 0.0028$).

Solution (mg/L)		Solid (mg/kg)	
Initial	Equilibrium	C_s	C_s (predicted)*
C_i	C_e	C_s	C_s (predicted)*
9.351	5.491	224.6	217
9.351	5.650	215.0	223
3.740	2.026	102.7	100
3.740	2.059	100.7	101
1.496	0.7014	50.88	51.6
1.496	0.7023	50.83	51.6
0.5985	0.1975	23.77	24.6
0.5985	0.1984	23.72	24.6
0.2394	0.0549	10.67	9.60
0.2394	0.0533	10.65	9.37
0.09576	0.0188	4.57	3.72
0.00576	0.0185	4.59	3.67
0.03830	0.0076	1.77	1.57
0.03830	0.0079	1.75	1.63
0.00000	0.0000	0.00	0.00

*From eq 8: $C_s = \frac{180.3C_e}{1 + 4.943C_e} + 33.15C_e$

Table A13. TNT sorption on Wyoming bentonite (100 mg/6 mL; 10°C; pH 8.8).

Solution (mg/L)		Solid (mg/kg)	
Initial C_i	Equilibrium C_e	C_s	C_s (predicted)*
9.281	7.07	132.3	132
9.281	7.08	131.7	132
3.173	2.72	59.7	59.3
3.173	2.74	59.1	59.3
1.485	1.028	27.0	26.9
1.485	1.028	27.0	26.9
0.594	0.402	11.4	12.1
0.594	0.395	11.8	11.9
0.238	0.149	5.32	4.89
0.238	0.148	5.38	4.86
0.0950	0.0577	2.25	1.97
0.0950	0.0573	2.37	1.95
0.0380	0.0231	0.902	0.799
0.0380	0.0261	0.718	0.902

*From eq 8: $C_s = \frac{19.07C_e}{1 + 0.8303C_e} + 15.88C_e$

Table A14. TNT desorption on Quik-Gel (10°C; pH 8.4; average of duplicates).

Solution (mg/L)		Solid (mg/kg)	
Initial C_i	Equilibrium C_e	C_s	C_s (predicted)*
3.70	2.23	87.0	76.6
1.66	1.04	37.0	41.6
0.704	0.449	15.6	19.9
0.286	0.197	5.35	9.21
0.125	0.0759	2.94	3.65
0.0539	0.0328	1.27	1.59
0.0257	0.0129	0.767	0.630
0.0000	0.0000	0.000	0.000

*From eq 8: $C_s = \frac{32.37C_e}{1 + 0.3688C_e} + 16.58C_e$

Table A15. TNT desorption on Aqua-Gel (10°C; pH 7.0; 0.05 M NaCl; $I = 0.0455$).

Solution (mg/L)		Solid (mg/kg)	
Initial C_i	Equilibrium C_e	C_s	C_s (predicted)*
4.496	2.627	111	117
4.496	2.689	107	119
2.046	0.969	64.2	59.9
2.046	0.996	62.6	60.9
0.9074	0.372	32.0	33.9
0.9074	0.375	31.8	34.1
0.4288	0.151	16.6	18.9
0.4288	0.149	16.8	18.7
0.1827	0.0625	7.22	9.55
0.1827	0.0540	7.73	8.44
0.0787	0.0227	3.19	3.89
0.0314	0.0105	1.25	1.87
0.0000	0.0000	0.00	0.00

*From eq 8: $C_s = \frac{153.1C_e}{1 + 4.281C_e} + 32.04C_e$

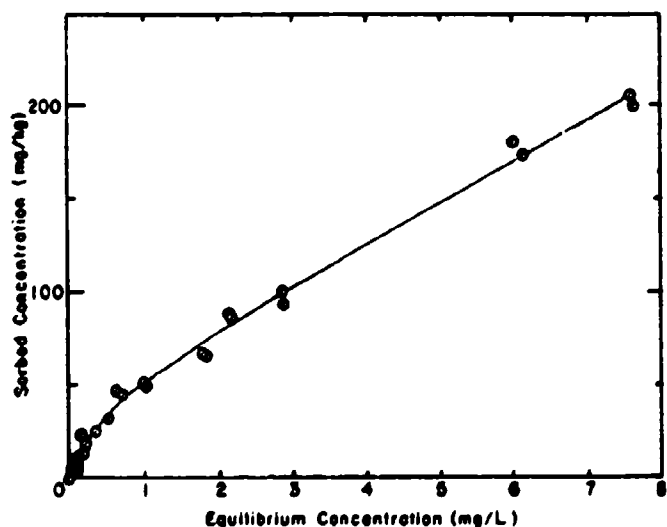


Figure A1. TNT sorption on Quik-Gel from well water (composite).

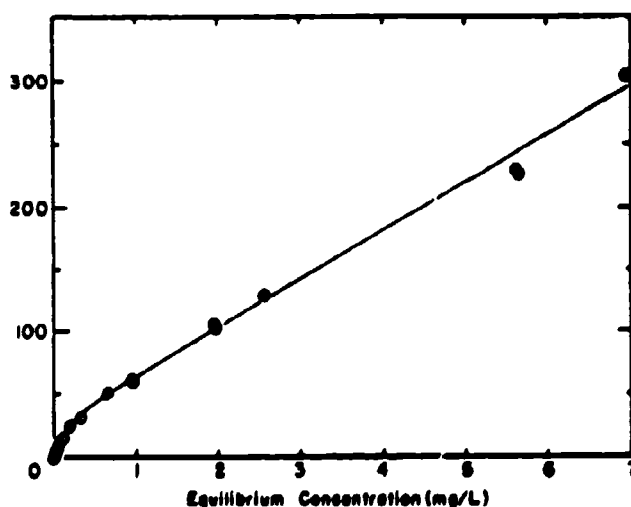


Figure A2. TNT sorption on Aqua-Gel from well water (composite).

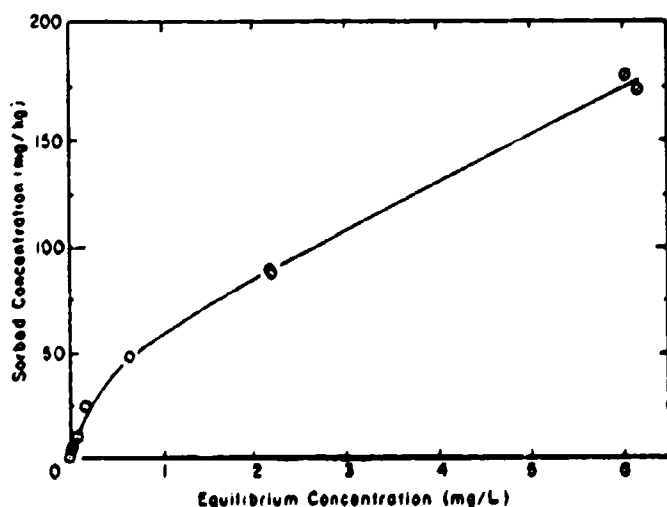


Figure A3. TNT sorption on Quik-Gel from well water (100 mg/mL).

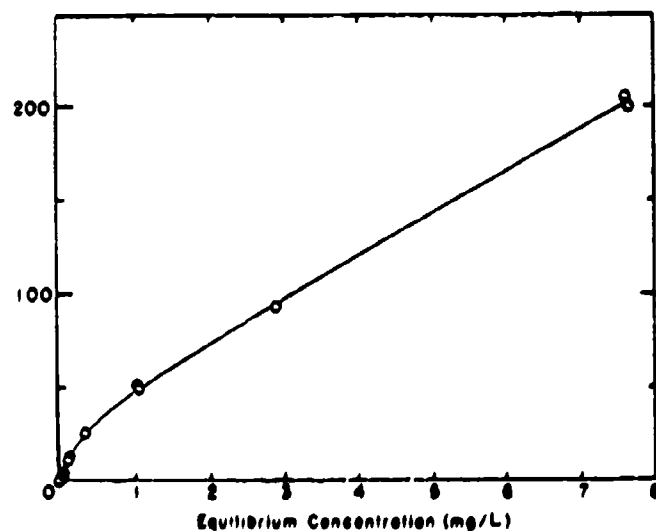


Figure A4. TNT sorption on Quik-Gel from well water (50 mg/6 mL).

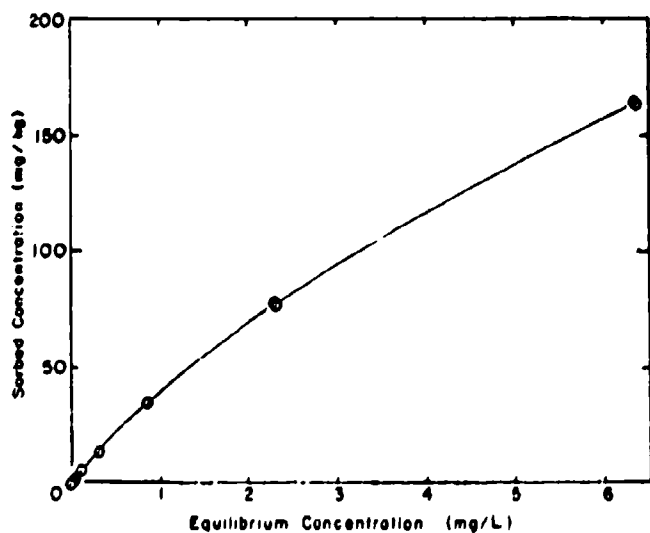


Figure A5. TNT sorption on Quik-Gel from 0.05 M NaCl (100 mg/mL).

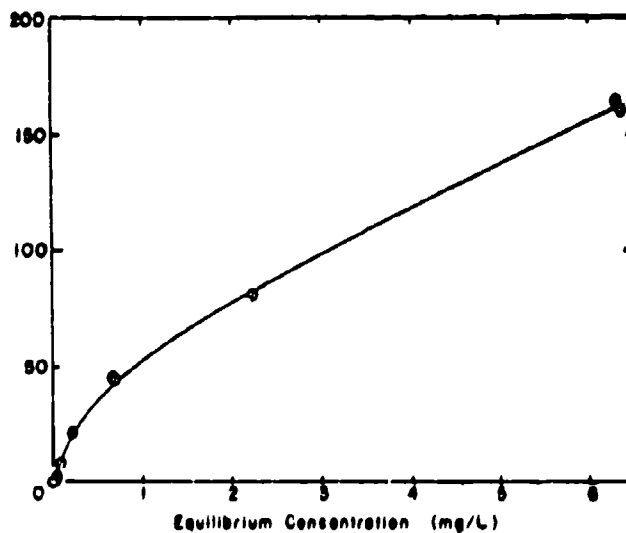


Figure A6. TNT sorption on Quik-Gel from distilled water (100 mg/6 mL).

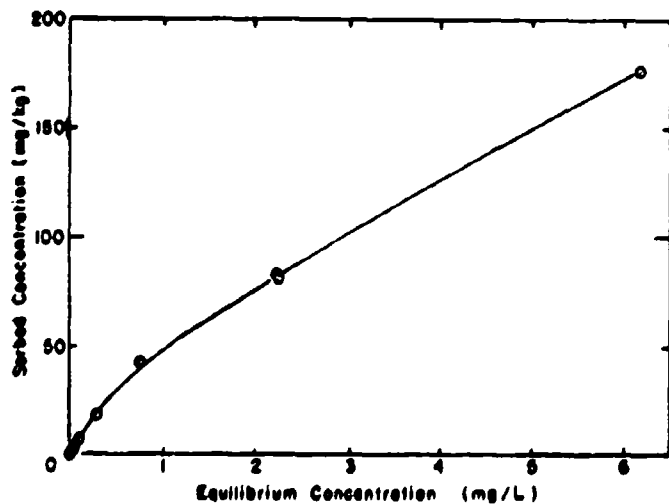


Figure A7. TNT sorption on Qul-Gel from well water (24°C; 100 mg/6 mL).

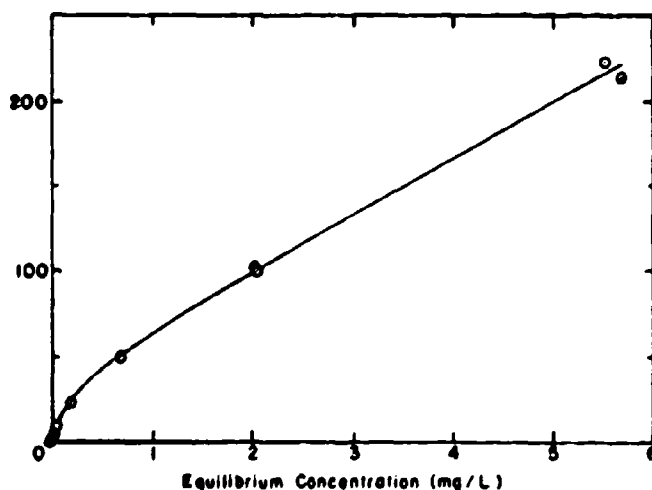


Figure A8. TNT sorption on Aqua-Gel from well water (100 mg/6 mL).

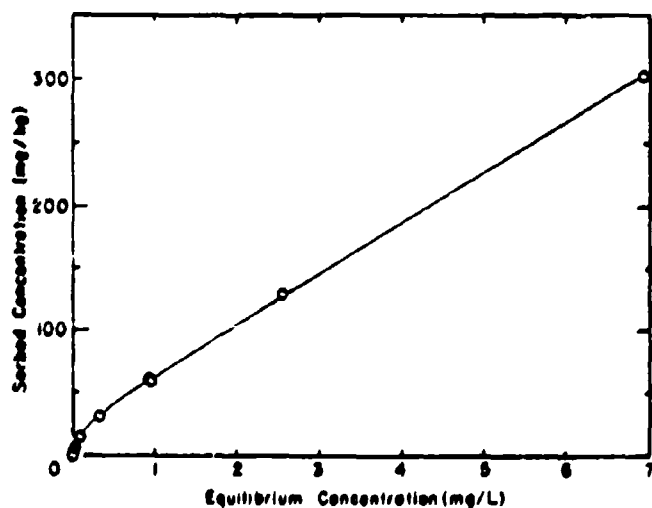


Figure A9. TNT sorption on Aqua-Gel from well water (50 mg/6 mL).

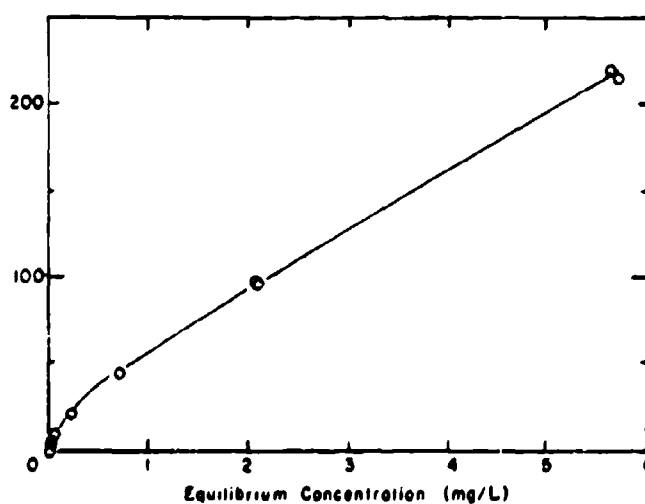


Figure A10. TNT sorption on Aqua-Gel from 0.05 M $MgCl_2$ (100 mg/6 mL).

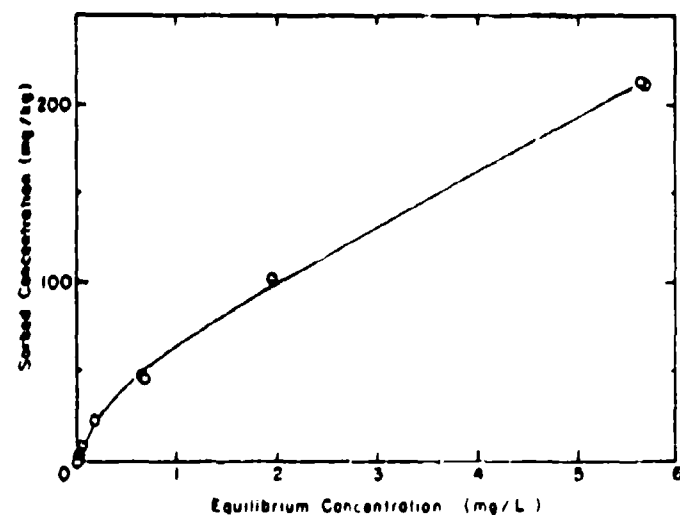


Figure A11. TNT sorption on Aqua-Gel from 0.05 M $NaCl$ (100 mg/6 mL).

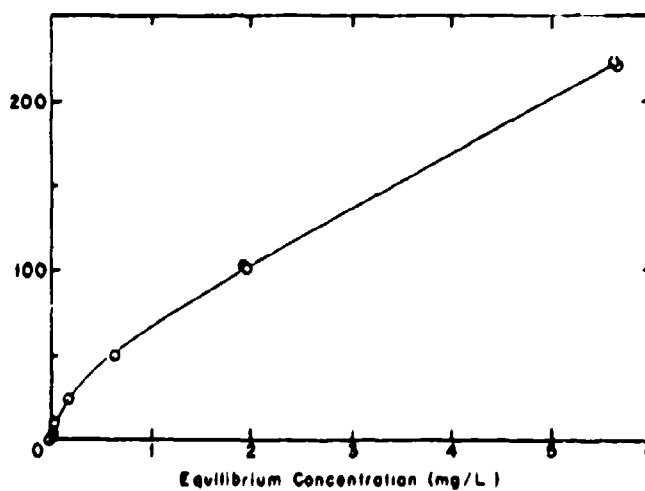


Figure A12. TNT sorption on Aqua-Gel from distilled water (100 mg/6 mL).

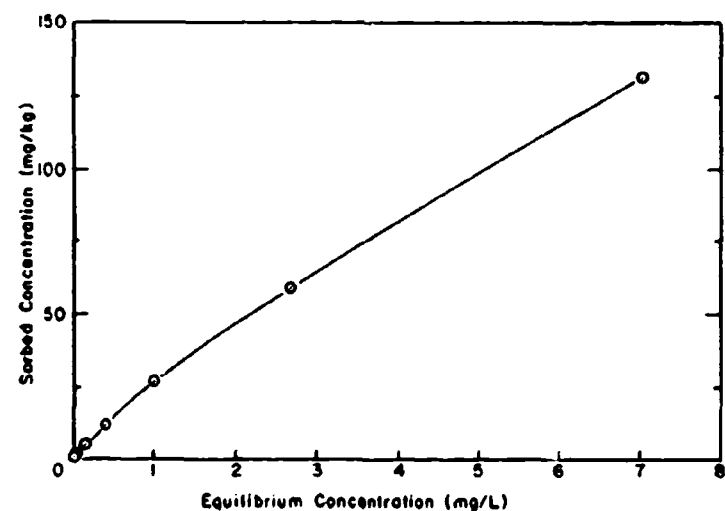


Figure A13. TNT sorption on Wyoming bentonite from well water (100 mg/6 mL).

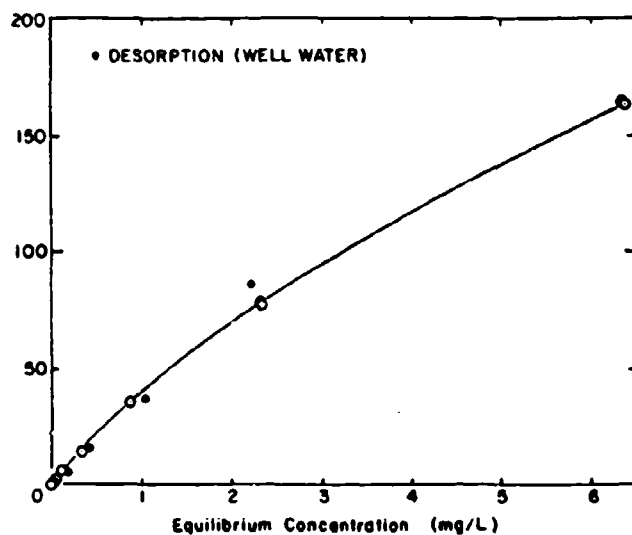


Figure A14. TNT sorption/desorption on Quik-Gel from 0.05 M NaCl (100 mg/6 mL).

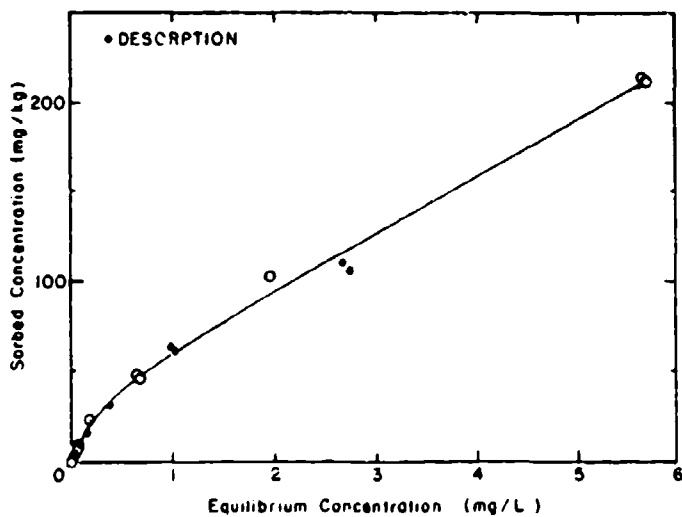


Figure A15. TNT sorption/desorption on Aqua-Gel from 0.05 M NaCl.

APPENDIX B: RESULTS FOR DNT

Table B1. DNT sorption on Aqua-Gel (100 mg/6 mL; 10°C).

Solution (mg/L)		Solid (mg/kg)	
Initial C_i	Equilibrium C_e	C_s	C_s (predicted)*
2.492	1.479	60.9	61.9
2.492	0.457	62.1	61.2
0.9969	0.5075	29.4	29.9
0.9969	0.4899	30.4	29.3
0.3987	0.1580	14.4	14.9
0.3987	0.1590	14.4	14.9
0.1595	0.0463	6.78	6.27
0.1595	0.0483	6.66	6.48
0.0638	0.0170	2.80	2.67
0.0638	0.0169	2.81	2.65
0.0000	0.0000	0.00	0.00

*From eq 8: $C_s = \frac{143.5C_e}{1+8.013C_e} + 30.68C_e$

Table B2. DNT sorption on Quik-Gel (100 mg/6 mL; 10°C).

Solution (mg/L)		Solid (mg/kg)	
Initial C_i	Equilibrium C_e	C_s	C_s (predicted)*
2.395	1.499	53.9	53.3
2.395	1.514	53.0	53.6
0.9579	0.5008	27.4	26.9
0.9579	0.5074	27.1	27.2
0.3832	0.1808	12.06	12.6
0.3832	0.1841	11.86	12.8
0.1533	0.0596	5.62	4.75
0.1533	0.0596	5.62	4.75
0.0613	0.0214	2.63	1.79
0.0613	0.0171	1.36	1.44

*From eq 8: $C_s = \frac{70.55C_e}{1+1.689C_e} + 15.58C_e$

Table B3. DNT sorption on Quik-Gel (200 mg/6 mL; 10°C).

Solution (mg/L)		Solid (mg/kg)	
Initial C_i	Equilibrium C_e	C_s	C_s (predicted)*
2.395	1.025	41.2	41.1
2.395	1.030	41.0	41.2
0.9579	0.3214	19.1	19.2
0.9579	0.3150	19.3	18.9
0.3832	0.1110	8.12	8.18
0.3832	0.1132	8.06	8.32
0.1533	0.0485	3.15	3.87
0.1533	0.0407	3.38	3.28
0.0613	0.0158	1.36	1.32
0.0613	0.0094	1.54	0.792

*From eq 8: $C_s = \frac{69.49C_e}{1+1.833C_e} + 15.97C_e$

Table B4. DNT desorption on Quik-Gel (200 mg/6 mL; 10°C).

Solution (mg/L)		Solid (mg/kg)	
Initial C_i	Equilibrium C_e	C_s	C_s (predicted)*
1.665	0.636	30.9	30.2
0.736	0.259	14.3	15.7
0.301	0.100	6.01	7.06
0.123	0.0378	2.56	2.87
0.0537	0.0170	1.10	1.32

*From eq 8: $C_s = \frac{62.24C_e}{1+1.674C_e} + 17.35C_e$

Table B5. DNT sorption on Aqua-Gel (200 mg/6 mL; 10°C).

Solution (mg/L)		Solid (mg/kg)	
Initial C_i	Equilibrium C_e	C_i	C_e (predicted)*
2.385	0.913	44.16	44.6
2.385	0.900	44.35	44.1
0.954	0.270	20.52	21.2
0.954	0.257	20.91	20.6
0.3816	0.0682	9.402	9.76
0.3816	0.0644	9.516	9.41
0.3816	0.0604	9.636	9.03
0.3816	0.0595	9.663	8.94
0.1526	0.0232	3.882	4.39
0.1526	0.0232	3.882	4.51
0.0000	0.0000	0.000	0.00

*From eq 8: $C_i = \frac{212.7C_e}{1+13.66C_e} + 33.01C_e$

Table B6. DNT desorption on Aqua-Gel (200 mg/6 mL; 19°C).

Solution (mg/L)		Solid (mg/kg)	
Initial C_i	Equilibrium C_e	C_i	C_e (predicted)*
1.66	0.614	31.3	33.4
1.67	0.585	32.5	32.3
0.741	0.200	16.2	17.1
0.751	0.198	16.6	17.0
0.327	0.0576	8.08	8.40
0.330	0.0554	8.24	8.20
0.135	0.0251	3.30	4.70
0.134	0.0185	3.47	3.69

*From eq 8: $C_i = \frac{212.7C_e}{1+13.66C_e} + 33.01C_e$

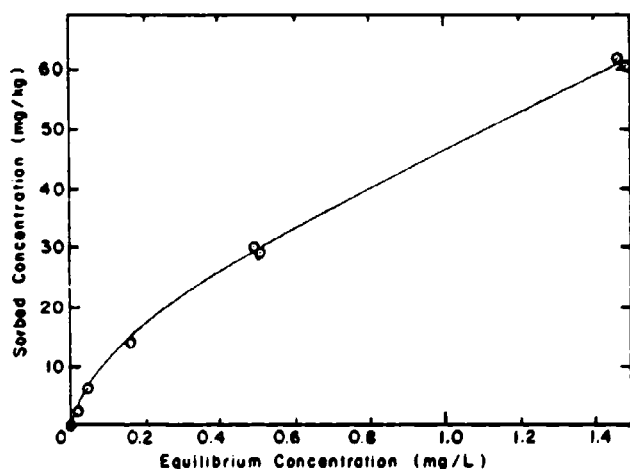


Figure B1. DNT sorption on Aqua-Gel from well water (100 mg/6 mL).

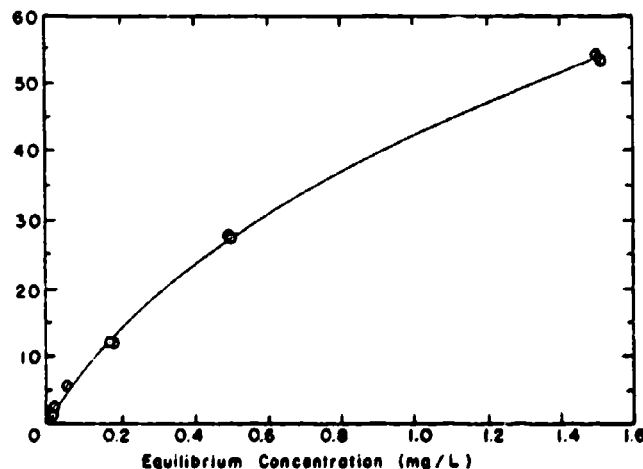


Figure B2. DNT sorption on Quik-Gel from well water (100 mg/6 mL).

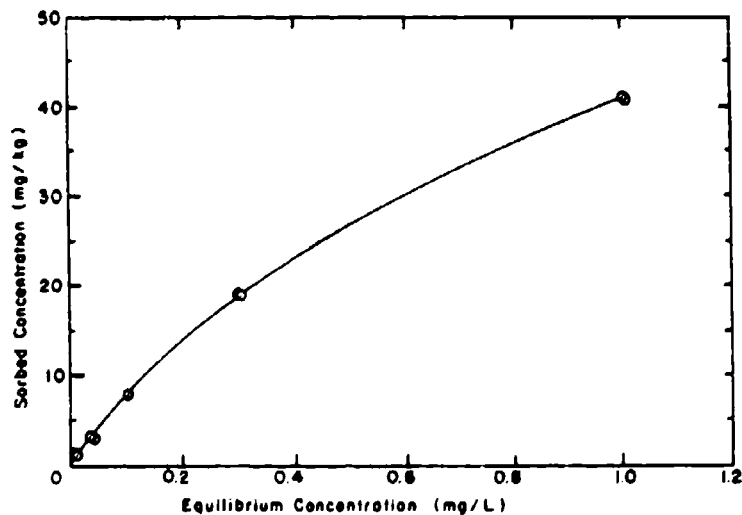


Figure B3. DNT sorption on Quik-Gel from well water (200 mg/6 mL).

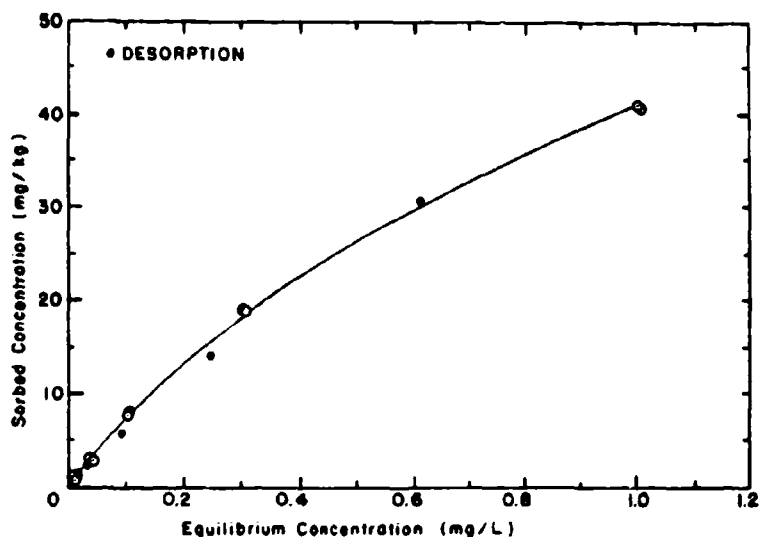


Figure B4. DNT sorption/desorption on Quik-Gel from well water (200 mg/6 mL).

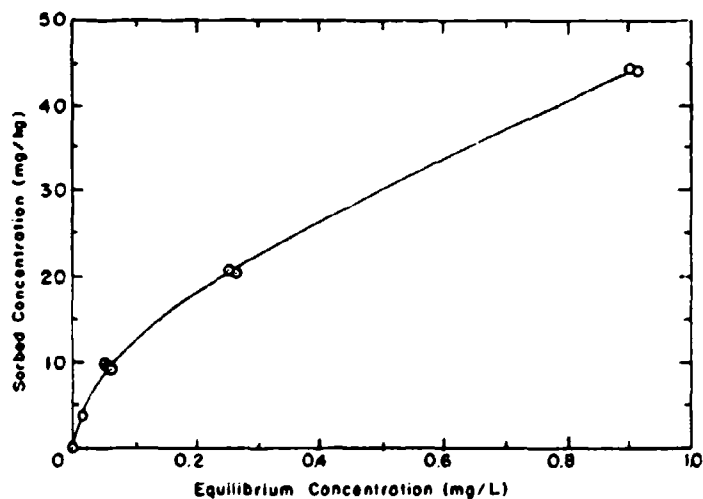


Figure B5. DNT sorption on Aqua-Gel from well water (200 mg/6 mL).

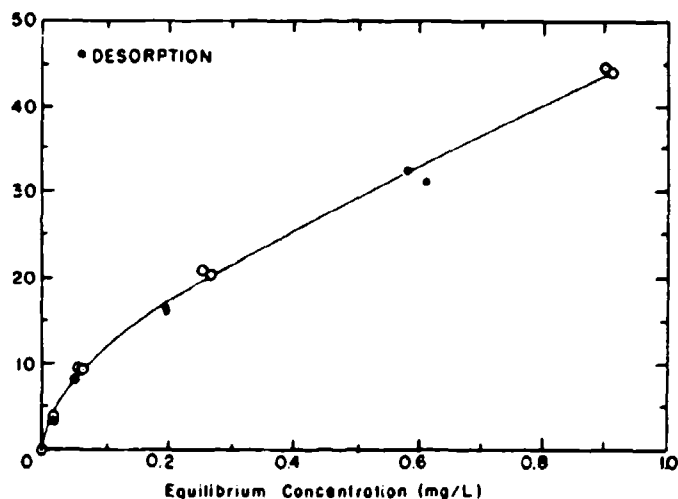


Figure B6. DNT sorption/desorption on Aqua-Gel from well water (200 mg/6 mL).

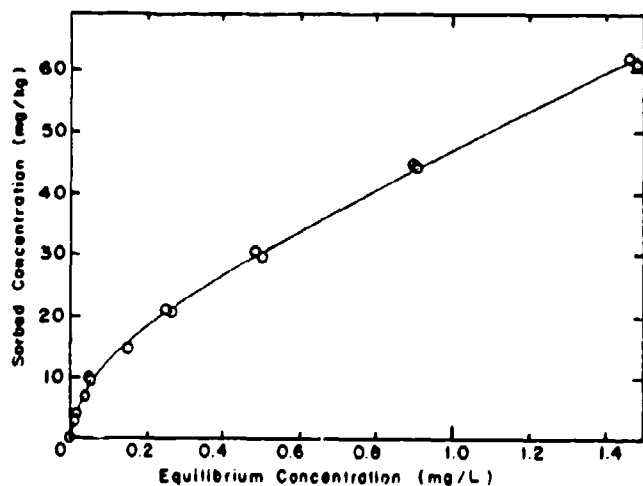


Figure B7. DNT sorption on Aqua-Gel from well water (composite).

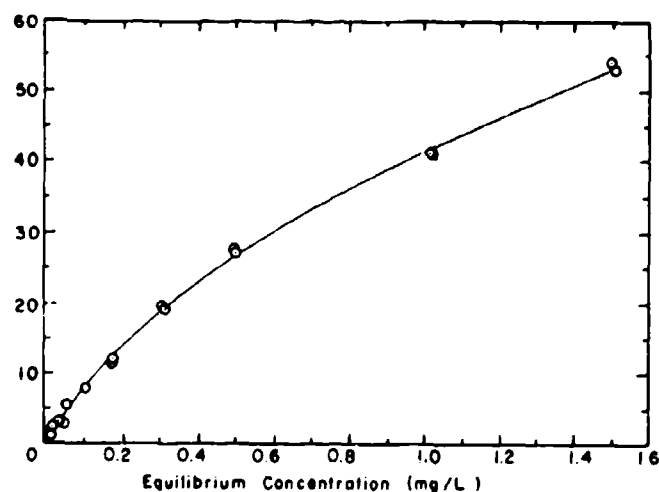


Figure B8. DNT sorption on Quik-Gel from well water (composite).

APPENDIX C: RESULTS FOR RDX

Table C1. RDX sorption on Aqua-Gel (200 mg/6 mL; 10°C).

Solution (mg/L)		Solid (mg/kg)	
Initial	Equilibrium		
C_i	C_e	C_s	C_s (predicted)*
2.870	2.356	15.4	15.9
2.870	2.331	16.2	15.7
1.148	0.921	6.71	6.22
0.459	0.380	2.33	2.57
0.459	0.388	2.10	2.62
0.184	0.155	0.879	1.05
0.184	0.152	0.970	1.03
0.0735	0.0645	0.273	0.436
0.0294	0.0252	0.126	0.170
0.0294	0.0263	0.093	0.177

*From eq 6: $C_s = 6.752C_e$.

Table C2. RDX sorption on Aqua-Gel (400 mg/6 mL; 10°C).

Solution (mg/L)		Solid (mg/kg)	
Initial	Equilibrium		
C_i	C_e	C_s	C_s (predicted)*
2.660	1.849	12.2	11.8
2.660	1.879	11.7	12.0
0.426	0.299	1.91	1.91
0.426	0.316	1.65	2.02
0.170	0.135	0.524	0.863
0.170	0.121	0.733	0.773
0.068	0.0476	0.306	0.304
0.068	0.0364	0.474	0.233

*From eq 6: $C_s = 6.389C_e$.

Table C3. RDX sorption on Quik-Gel (200 mg/6 mL; 10°C).

Solution (mg/L)		Solid (mg/kg)	
Initial	Equilibrium		
C_i	C_e	C_s	C_s (predicted)*
2.825	2.43	11.79	12.0
1.130	0.950	5.40	4.67
0.425	0.384	1.21	1.89
0.181	0.158	0.680	0.777
0.0723	0.0648	0.224	0.319

*From eq 6: $C_s = 4.920C_e$.

Table C4. RDX sorption on Quik-Gel (400 mg/6 mL; 10°C).

Solution (mg/L)		Solid (mg/kg)	
Initial	Equilibrium		
C_i	C_e	C_s	C_s (predicted)*
14.78	10.60	61.6	61.4
14.78	10.63	61.2	61.6
5.913	4.23	25.1	24.5
5.913	4.26	24.7	24.7
0.9460	0.7105	3.50	4.12
0.9460	0.7087	3.52	4.10
0.3784	0.282	1.37	1.63
0.1514	0.120	0.469	0.695
0.1514	0.127	0.365	0.736
0.0605	0.0469	0.204	0.272

*From eq 6: $C_s = 5.792C_e$.

Table C5. RDX desorption on Quik-Gel (400 mg/6 mL; 10°C).

Solution (mg/L)		Solid (mg/kg)	
Initial	Equilibrium		
C_i	C_e	C_s	C_s (predicted)*
8.446	5.578	42.3	34.2
8.446	5.607	41.9	34.4
0.519	0.350	2.51	2.14
0.519	0.361	2.35	2.21
0.211	0.147	0.904	0.901
0.211	0.144	0.953	0.882

*From eq 6: $C_s = 6.126C_e$.

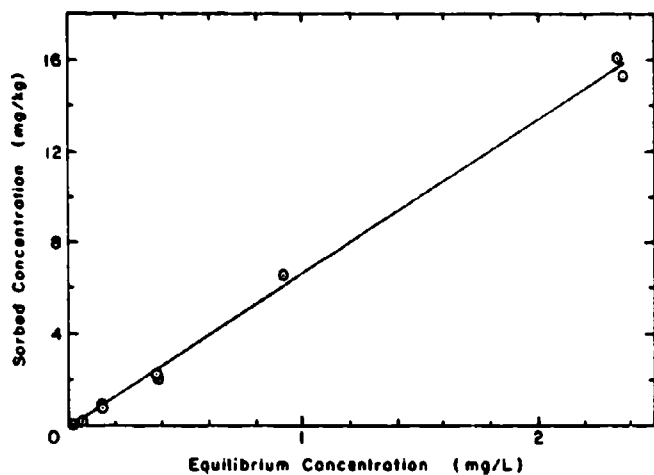


Figure C1. RDX sorption on Aqua-Gel from well water (200 mg/6 mL).

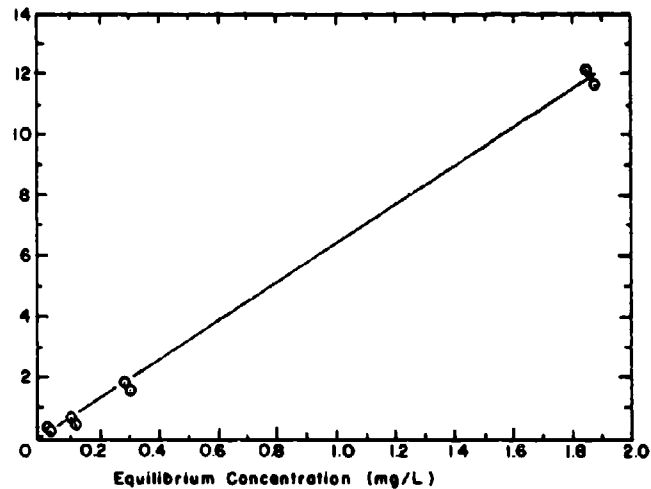


Figure C2. RDX sorption on Aqua-Gel from well water (400 mg/6 mL).

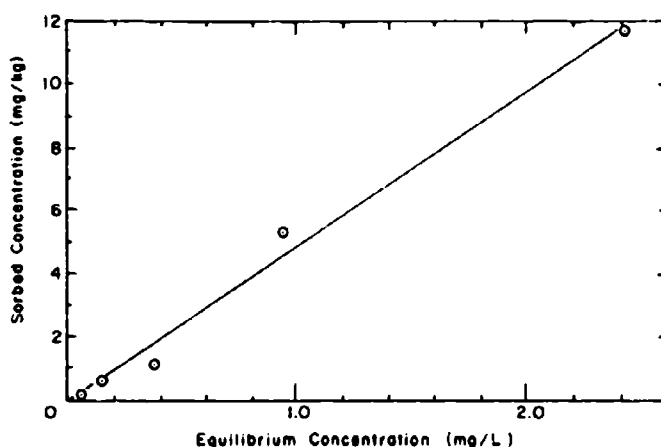


Figure C3. RDX sorption on Quik-Gel from well water (200 mg/6 mL).

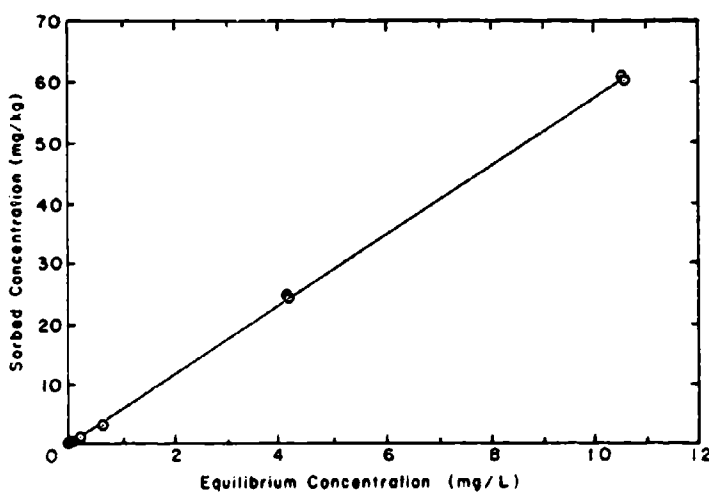


Figure C4. RDX sorption on Quik-Gel from well water (400 mg/6 mL).

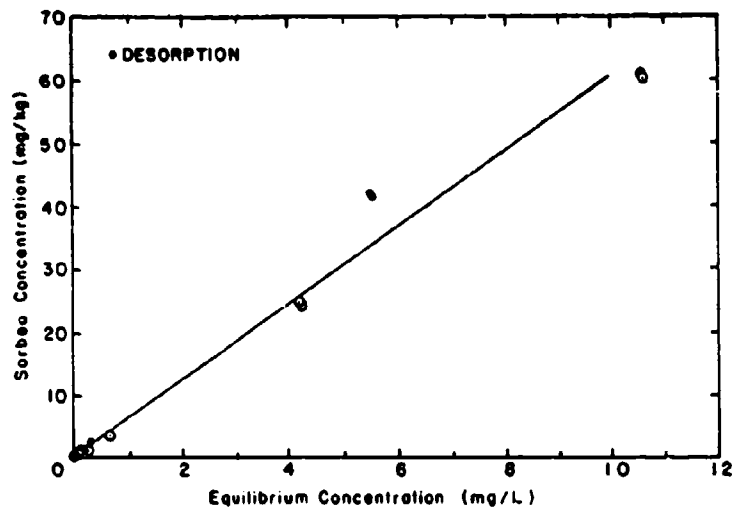


Figure C5. RDX sorption/desorption on Quik-Gel from well water (400 mg/6 mL).

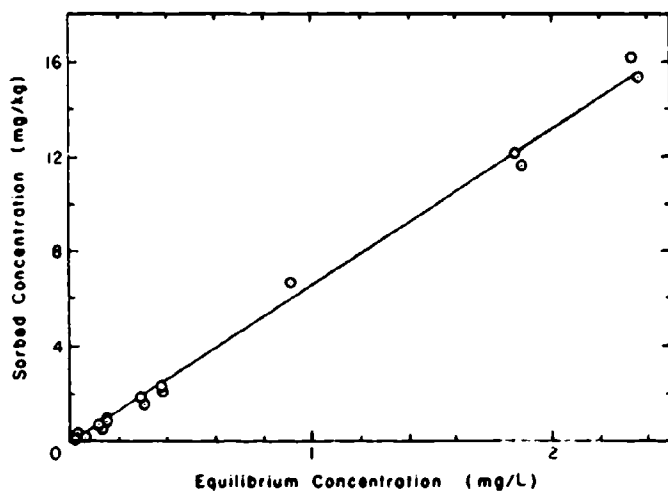


Figure C6. RDX sorption on Aqua-Gel from well water (composite).

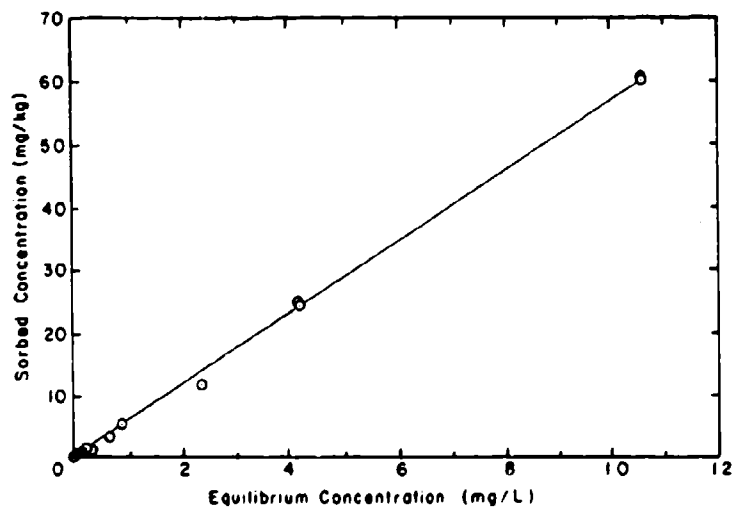


Figure C7. RDX sorption on Quik-Gel from well water (composite).

APPENDIX D: RESULTS FOR HMX

Table D1. HMX sorption on Aqua-Gel (10°C).

Solution (mg/L)		Solid (mg/kg)	
Initial C_i	Equilibrium C_e	C_s	C_s (predicted)*
200 mg/6 mL			
0.294	0.220	2.22	1.95
0.294	0.231	1.89	2.05
0.117	0.0801	1.09	0.710
0.117	0.0653	0.937	0.756
400 mg/6 mL			
0.259	0.169	1.35	1.50
0.259	0.173	1.29	1.53
0.0415	0.0267	0.222	0.237

*From eq 6: $C_s = 8.867 C_e$.

Table D2. HMX sorption on Quik-Gel (10°C).

Solution (mg/L)		Solid (mg/kg)	
Initial C_i	Equilibrium C_e	C_s	C_s (predicted)*
200 mg/6 mL			
0.321	0.255	1.97	3.38
0.128	0.110	0.54	1.46
400 mg/6 mL			
1.89	1.03	12.68	13.6
1.89	0.949	13.87	12.6
0.756	0.380	5.61	5.03
Desorption			
1.30	0.5476	8.073	7.53†
1.30	0.5476	8.073	7.53

*From eq 6: $C_s = 13.25 C_e$.

†From eq 6: $C_s = 13.75 C_e$.

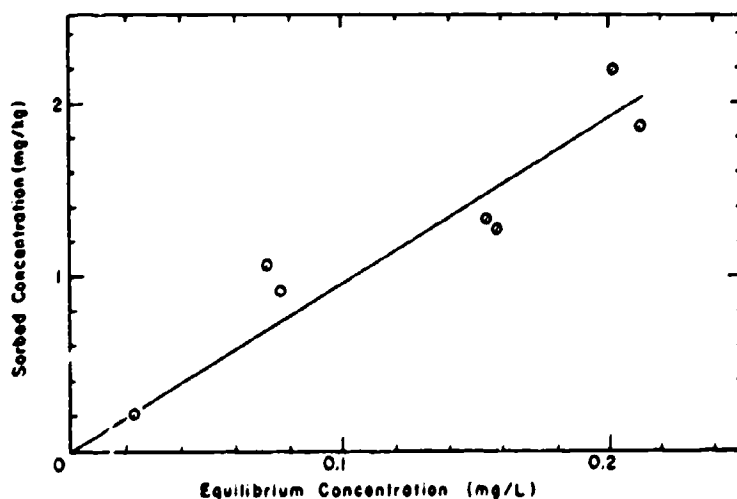


Figure D1. HMX sorption on Aqua-Gel from well water (composite).

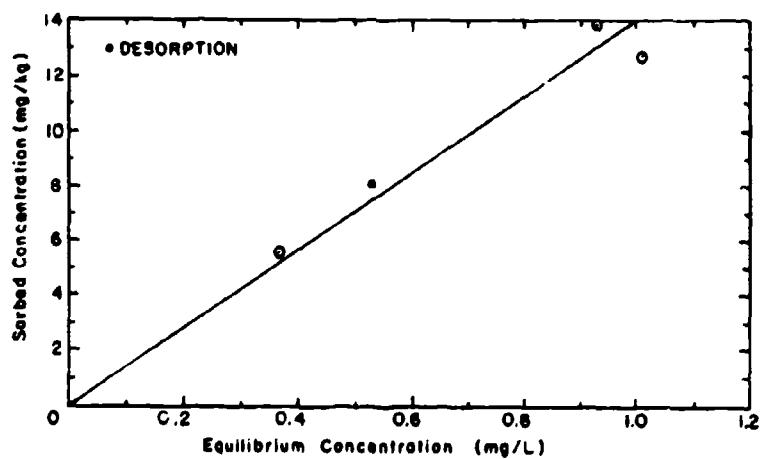


Figure D2. HMX sorption/desorption on Quik-Gel from well water (400 mg/6 mL).

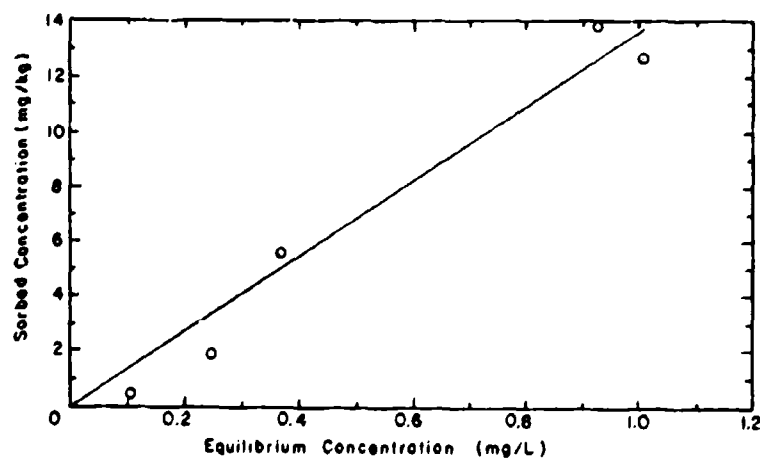


Figure D3. HMX sorption on Quik-Gel from well water (composite).

APPENDIX E: CHARACTERISTICS OF QUIK-GEL, AQUA-GEL AND WELL WATER

Table E1. Physical and chemical properties of Quik-Gel.

Quik-Gel is a high-yield, sodium-base montmorillonite Western Bentonite. It is nontoxic and has a specific gravity of 2.5. The physical and chemical properties of the bentonite mined in the area where Quik-Gel is produced are listed below:

X-ray analysis

85% Montmorillonite
5% Quartz
5% Feldspar
2% Cristobalite
2% Illite
1% Calcium and gypsum

Chemical analysis

SiO ₂	55.44%
Al ₂ O ₃	20.14%
Fe ₂ O ₃	3.67%
CaO	0.49%
MgO	2.49%
Na ₂ O	2.76%
K ₂ O	0.60%
Bound water	5.50%
Moisture at 220 °F	8.00%
TOTAL	99.09%

In addition to drilling mud applications, other common uses for Western Bentonite are: binder for cattle feed pellets, water clarification, body powders, cosmetics, etc.

Quik-Gel contains a small amount of nontoxic organic polymer of the type approved by FDA for use in packages for food and other consumer products.

Table E3. Physical and chemical characteristics of well water.

pH = 7.3
Total suspended solids = <0.1 mg/L
Total dissolved solids = 235 mg/L
Specific conductance = 331 µmhos
Na⁺ = 94 mg/L
Mg⁺⁺ = 13 mg/L
Ca⁺⁺ = 167 mg/L
TOC = 0.7 mg/L

Total suspended solids, total dissolved solids, specific conductance and pH were determined by Standard Methods (APHA-AWWA-WPCF 1980). Na, Ca and Mg were analyzed by Furnace AA using Perkin-Elmer Model 703AA and HGA-2200 graphite furnace. The Na, Mg and Ca analyses were performed on a different sample. Total organic carbon (TOC) was determined on an OIC Organic Carbon Analyzer using the persulfate oxidation (ampoule) method.

Table E2. Physical and chemical properties of Aqua-Gel.

X-ray analysis

85% Montmorillonite
5% Quartz
5% Feldspar
2% Cristobalite
2% Illite
1% Calcium and gypsum

Screen analysis (Ground material)

99.6% through 100 mesh
91.4% through 200 mesh
76.2% through 325 mesh

Chemical analysis

SiO ₂	55.44%
Al ₂ O ₃	20.14%
Fe ₂ O ₃	3.67%
CaO	0.49%
MgO	2.49%
Na ₂ O	2.76%
K ₂ O	0.60%
Bound water	5.50%
Moisture at 220 °F	8.00%
TOTAL	99.09%

Miscellaneous properties

Specific gravity of dried material	2.79
Specific gravity of natural material	2.00
Fusion temperature	2444 °F
Weight of dried bulk unpulverized	71 lb/ft ³
Weight of pulverized material	61 lb/ft ³
Weight of crude, crushed, undried material	80 lb/ft ³
Refractive index	1.557
pH of 6% water suspension	8.8

Foundry properties

Green Comp. strength, psi	6.3
Dry Comp. strength, psi	65.0
Green permeability	215

A facsimile catalog card in Library of Congress MARC format is reproduced below.

Leggett, Daniel C.

Sorption of military explosive contaminants on bentonite drilling muds / by Daniel C. Leggett. Hanover, N.H.: Cold Regions Research and Engineering Laboratory; Springfield, Va.: available from National Technical Information Service, 1985.

iv, 40 p., illus., 28 cm. (CRREL Report 85-18.)

Prepared for U.S. Army Toxic and Hazardous Materials Agency, Aberdeen Proving Ground, Maryland.

Bibliography: p. 14.

1. DNT. 2. Drilling. 3. Explosives. 4. HMX. 5. RDX. 6. TNT. I. United States. Army. Corps of Engineers. II. Cold Regions Research and Engineering Laboratory, Hanover, N.H. III. Series: CRREL Report 85-18.